

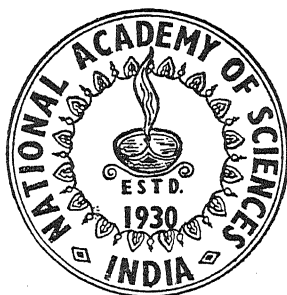
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PART VI

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PART VI]

SECTION A

[VOL. XXVII

INFLUENCE OF CALCIUM PHOSPHATE
INCORPORATED WITH ENERGY-RICH
MATERIALS ON NITROGEN
FIXATION—PART I

BY S. S. SHARMA AND A. K. BHATTACHARYA

(*Department of Chemistry, University of Saugar*)

Read at the 27th Annual Session of the Academy held at the University
of Jabalpur on 27th December, 1957

THE use of phosphates as fertilisers is well known. Dhar¹ and other workers have reported that in presence of phosphates the carbonaceous substances undergo more rapid oxidation and thus fixation of atmospheric nitrogen in soil is increased. Bear² has remarked that "within limits phosphate fertilisers together with potash salts and lime can be substituted for nitrogen fertilisers". In the present communication the results of the influence of calcium phosphate, alone and in combination with organic energy-rich materials like glucose and starch, on the fixation of atmospheric nitrogen in soil are recorded.

EXPERIMENTAL

The soil used in these experiments was obtained from a cultivated field near the University campus. Different sets of soil containing 0.5% of each of the above-mentioned ammendments, alone and in combination, as shown in Table I, were taken in glass jars and regularly exposed to sunlight for about 8 hours every day, for a period of 7 months. The moisture content was kept constant at approximately 20% by the addition of distilled water. The mixtures were stirred on alternate days to facilitate aeration. Every month soil samples were taken out, air-dried, crushed and sieved through 0.5 mm. sieve for the estimations of organic carbon and total nitrogen. Organic carbon was estimated by Walkley and Black's

method.³ Total nitrogen was estimated by the Kjeldahl's method.⁴ The ammoniacal nitrogen was estimated by Mclean and Robinson's method⁵ and Nitrate nitrogen by that of Piper.⁶ The total carbonates were estimated by the method given by Piper.⁷ Soil suspensions were prepared by taking soil : water ratio of 1:5 and shaking mechanically for one hour for the measurements of conductivity and pH values using Dörañ's conductivity bridge and Beckmann glass electrode pH meter.

RESULTS AND DISCUSSION

The chemical analysis of the soil used:

Ammoniacal nitrogen	0.0006%
Nitrate nitrogen	0.0019%
Total nitrogen	0.056%
Organic carbon	0.454%
Loss on ignition	6.54%
Total carbonates	7.0%
Sp. conductivity at 30° C.	9.52×10^{-5} mhos
pH	8.5

TABLE I

Set No.	Composition
1	Soil + Glucose
2	Soil + Starch
3	Soil + Calcium phosphate
4	Soil + Calcium phosphate + Glucose
5	Soil + Calcium phosphate + Starch

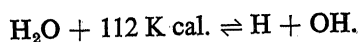
TABLE II

Period of exposure (days)	Organic carbon (%)	Carbon oxidised (%)	Total nitrogen (%)	Increase in nitrogen (%)
Set 1	0	0.654	0.056	
	210	0.410	0.077	0.021
Set 2	0	0.676	0.056	
	210	0.423	0.075	0.019
Set 3	0	0.454	0.056	
	210	0.398	0.065	0.009
Set 4	0	0.654	0.056	
	210	0.366	0.095	0.039
Set 5	0	0.676	0.056	
	210	0.378	0.094	0.038

From the results it is seen that in all cases the carbon content of the system decreased while the nitrogen content increased. The carbonaceous material is oxidised more when calcium phosphate is added along with organic energy-rich materials with greater increase in nitrogen. This shows, therefore, that when energy-rich materials are allowed to undergo slow oxidation in soil in presence of sunlight and moisture considerable amount of nitrogen fixation takes place. Even calcium phosphate, when alone, resulted in the oxidation of carbon and increase in nitrogen to a considerable extent. Dhar has explained the phenomenon of photochemical nitrogen fixation as analogous to photosynthesis. According to him, when the energy-rich materials like glucose, starch, etc., undergo oxidation on the surface of soil they liberate large amount of energy as indicated by the following equation:



The energy thus liberated is much more than the energy required for the decomposition of water molecule into $\text{H} + \text{OH}$.



The atomic hydrogen thus formed combines with molecular nitrogen perhaps absorbed on the surface of soil and forms ammonia. The ammonia thus formed undergoes further oxidation into nitrite and nitrate.

The conclusion derived from the above experiments is that the fixation of atmospheric nitrogen by the addition of organic matter to the alkali soil is greatly enhanced by the presence of calcium phosphate. Therefore, the inclusion of cheap organic matter along with phosphates offer a rapid method of improving the fertility of alkali soils which are poor in nitrogen and carbon.

The authors are indebted to the King Edward Memorial Society for the award of a research scholarship to one of them (S. S. S.) which enabled them to carry out the above work.

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THE INFLUENCE OF CHEMICAL CONSTITUTION OF THE ROTATORY POWER OF OPTICALLY ACTIVE COMPOUNDS

Cinchonidine Salts of Benzoic, *o*-, *m*- and *p*-Hydroxy Benzoic Acids

BY SAKTI PRASHAD BANERJEE AND M. S. MANHAS

(Department of Chemistry, University of Saugar)

Read at the 27th Annual Session of the Academy held at the University
of Jabalpur on 27th December, 1957

IN the preceding papers the author has discussed the rotatory dispersion of brucine and quinine salts of various aromatic acids. In the present work the author has prepared the cinchonidine salts and studied their rotatory dispersion in various non-ionising solvents. The author has also studied the effect of replacing the hydrogen atom by an electro-negative hydroxyl group in *o*-, *m*-, and *p*-positions of cinchonidine benzoate on the rotatory power.

EXPERIMENTAL

Cinchonidine benzoate.—It was prepared by mixing equimolecular quantities of cinchonidine and benzoic acid in boiling alcohol. The solution was filtered and allowed to cool whereby the salt separated out. It was then recrystallised out of ethyl alcohol as small white needles and dried in vacuum. Yield: 50%.

It is fairly soluble in pyridine and chloroform, less so in ethyl alcohol and methyl alcohol, sparingly soluble in acetone, water and ethyl acetate and practically insoluble in ether, petroleum ether, benzene and carbon tetrachloride, m.p. 208–09° C. Found: N, 6.30%, C, 74.80% and H, 6.54%. $C_{26}H_{28}O_3N_2$ requires N, 6.73%, C, 74.90% and H, 6.73%.

Cinchonidine-o-hydroxy benzoate.—This salt was prepared by mixing the solutions containing molar quantities of cinchonidine and *o*-hydroxy benzoic acid in boiling alcohol. The solution thus obtained after heating a little on water-bath was filtered. The filtrate was allowed to cool. On scratching with the glass rod the salt separated out. It was then repeatedly recrystallised out of ethyl alcohol as small white needles and dried in vacuum. Yield: 80%.

It is highly soluble in pyridine and chloroform, less so in methyl alcohol and ethyl alcohol, sparingly soluble in acetone, ethyl acetate and water and practically insoluble in ether, benzene, petroleum ether and carbon tetrachloride, m.p. 198–200° C. Found: N, 6.30%, C, 72.20% and H, 6.20%. $C_{26}H_{28}O_4N_2$ requires N, 6.48%, C, 72.22% and H, 6.48%.

Cinchonidine-m-hydroxy benzoate.—The salt was prepared by dissolving separately equimolecular proportions of cinchonidine and *m*-hydroxy benzoic acid in boiling alcohol. The two solutions were then mixed, heated for five minutes on a water-bath and filtered. The filtrate was allowed to evaporate to a syrupy mass. Sulphuric ether was then added to precipitate the salt. After filtering it was repeatedly recrystallised as small white needles out of a mixture of ethyl alcohol and ethyl acetate and dried in vacuum. Yield: 40%.

It is fairly soluble in pyridine, less so in methyl alcohol and ethyl alcohol, sparingly soluble in acetone, ethyl acetone and water and practically insoluble in ether, benzene, petroleum ether, carbon tetrachloride and chloroform, m.p. -184°C . Found: N, 6.00%, C, 72.00% and H, 6.48%. $\text{C}_{26}\text{H}_{28}\text{O}_4\text{N}_2$ requires N, 6.48%, C, 72.22% and H, 6.48%.

Cinchonidine-p-hydroxy benzoate.—It was prepared by mixing solutions containing molar proportion of cinchonidine and *p*-hydroxy benzoic acid in boiling alcohol. The solution thus obtained was filtered and the filtrate was evaporated to a syrupy mass. The salt was precipitated by the addition of sulphuric ether. It was then repeatedly recrystallised as small white rod-shaped crystals out of a mixture of acetone and ethyl alcohol and dried in vacuum. Yield: 55%.

It is highly soluble in pyridine, less so in methyl alcohol and ethyl alcohol, sparingly soluble in acetone, ethyl acetate and water and practically insoluble in ether, benzene, petroleum ether, carbon tetrachloride, and chloroform, m.p. $189-90^{\circ}$. Found: N, 6.20%, C, 7.190% and H, 6.39%. $\text{C}_{26}\text{H}_{28}\text{C}_4\text{N}_2$ requires N, 6.48%, C, 72.22% and H, 6.48%.

NATURE OF ROTATORY DISPERSION

The rotatory dispersion of cinchonidine salts has been determined for eleven wavelengths from (6708 Å.U. to 4358 Å.U.) in various non-ionising solvents and the results are recorded in the tables. It is found to be "simple" as it obeys Drude's one term equation, $(\alpha) = (K_0/\lambda^2 - \lambda_0^2)$. In this equation K_0 , the "rotation constant," may be taken as the measure of absolute rotation for the wavelength of λ and λ_0 represents absorption band of its molecule in the ultraviolet region of the spectrum respectively.

The difference (O-C) between the observed rotation (O) and the calculated values (C) are of the order of casual experimental errors and are given in Tables III to VI.

THE EFFECT OF SOLVENT ON THE ROTATORY POWERS

Table I gives the values of $[\alpha]_{\text{D}}^{20}$.

From a study of Table I it will be observed that the sequence of rotatory power in various solvents is as follows:

(1) *Cinchonidine benzoate*.—Chloroform > methyl alcohol > ethyl alcohol > pyridine.

The order of the decreasing rotatory power runs parallel to the decreasing order of the dielectric constant of the solvents except for chloroform.

(2) *Cinchonidine-o-hydroxy benzoate*.—Chloroform > ethyl alcohol > methyl alcohol > pyridine.

This sequence is in the reverse order of their dielectric constants except for pyridine.

(3) *Cinchonidine-m-hydroxy benzoate*.—Methyl alcohol > ethyl alcohol > pyridine.

Here the order of decreasing rotatory power runs parallel to the decreasing order of the dielectric constants of the solvents.

TABLE I

The specific rotatory power of different cinchonidine salts in various non-ionising solvents

No.	Compound	$[\alpha]_{5461}^{20}$			
		Chloroform (5.2)*	Pyridine (12.4)	Ethyl alcohol (25.8)	Methyl alcohol (31.2)
1	Cinchonidine benzoate	.. -129.50 (31.16)†	-40.00 (8.96)	-98.18 (23.43)	-114.00 (29.68)
2	Cinchonidine- <i>o</i> -hydroxy benzoate	200.00 (50.18)	30.50 (6.759)	154.50 (40.58)	119.00 (31.78)
3	Cinchonidine- <i>m</i> -hydroxy benzoate	..	43.50 (10.72)	95.40 (22.35)	110.00 (28.06)
4	Cinchonidine- <i>p</i> -hydroxy benzoate	..	45.25 (11.93)	88.00 (20.07)	93.00 (21.79)

* The figures in the brackets refer to dielectric constants of solvents.

† The figures in the brackets refer to the rotation constant, K.

(4) *Cinchonidine-p-hydroxy benzoate*.—Methyl alcohol > ethyl alcohol > pyridine.

This sequence again runs parallel to the decreasing order of the dielectric constants of the solvents.

Incidentally it may be pointed out that the cinchonidine salts exhibit the maximum rotation in chloroform. In the previous papers while discussing the effect of solvent on the rotatory power of brucine and quinine salts it was found that brucine salts show the highest rotation in pyridine whereas the quinine salts invariably exhibit the highest rotation in chloroform. It is, therefore, apparent that compounds of similar constitution tends to behave similarly regarding their rotatory effect in different solvents. Thus it becomes evident that besides the dielectric constant of the solvent other factors may also be playing their part in determining the extent of rotation in a particular solvent.

EFFECT OF POSITION ISOMERISM ON THE ROTATORY POWER

In Table II the order of specific rotatory power of position isomerides in different non-ionising solvents for Hg 5461 line, is given, the order of K is also given. On comparing the values of $[\alpha]_{5461}^{20}$, the sequence of position isomerides in pyridine is $o < un < m < p$, in ethyl alcohol is $p < m < un < o$ and in methyl alcohol is $p < m < un < o$. Similar sequence is followed when the values of K, the rotation constant, are compared. These results are in complete agreement with Frankland's¹ "lover arm" hypothesis as well as Cohen's² rule.

TABLE II

Solvent		$[\alpha]_{5461}^{20}$	K
Pyridine	..	$o < un < m < p$	$o < un < m < p$
Ethyl alcohol		$p < m < un < o$	$p < m < un < o$
Methyl alcohol	..	$p < m < un < o$	$p < m < un < o$

TABLE III

Cinchonidine-p-hydroxybenzoate

Solvent	Pyridine		Ethyl alcohol		Methyl alcohol	
Concentration in gm./100 c.c.	2.00		0.50		0.50	
Calculated $[\alpha]$	$\frac{11.93}{\lambda^2 - 0.0396}$ $\lambda_0 0.1989$		$\frac{20.07}{\lambda^2 - 0.070}$ 0.2646		$\frac{21.79}{\lambda^2 - 0.0618}$ 0.2486	
Line	Obs. (O)	Cal. (C)	Obs. (O)	Cal. (C)	Obs. (O)	Cal. (C)
Li 6708	-29.35°	-29.07°	-52.72°	-52.83°	-56.00°	-56.24°
Cd 6438	32.25	31.83	57.27	58.28	61.00	61.79
Li 6104	35.25	35.84	66.36	66.37	70.00	70.13
Na 5893	38.75	38.79	72.72	72.43	76.00	76.37
Hg 5780	40.25	40.52	76.36	76.02	80.00	80.02
Hg 5461	45.25	46.14	88.00	87.98	93.00	92.19
Cd 5085	54.75	54.46	106.37	106.40	111.00	111.70
Cd 4799	62.50	62.50	125.45	125.10	129.00	129.20
Cd 4678	66.50	66.55	133.60	134.80	139.00	138.70
Li 4602	70.25	69.29	141.80	141.60	146.00	146.30
Hg 4358	167.30	167.30	170.00	170.00

TABLE IV
Cinchonidine-m-hydroxy benzoate

Solvent	Pyridine		Ethyl alcohol		Methyl alcohol	
Concentration in gm./100 c.c.	2.00		0.50		0.50	
Calculated $[\alpha]$	$\frac{10.72}{\lambda^2 - 0.0518}$ λ_0 0.2276		$\frac{22.35}{\lambda^2 - 0.064}$ 0.2529		$\frac{28.06}{\lambda^2 - 0.0431}$ 0.2144	
Line	Obs. (O)	Cal. (C)	Obs. (O)	Cal. (C)	Obs. (O)	Cal. (C)
Li 6708	-27.00°	-26.92°	-58.18°	-57.88°	-69.00°	-68.96°
Cd 6438	30.00	29.55	63.63	63.74	76.00	75.54
Li 6104	33.00	33.43	71.80	72.41	85.00	85.19
Na 5893	36.25	36.28	79.00	78.89	92.00	92.28
Hg 5780	37.75	37.96	82.72	82.69	96.00	96.42
Hg 5461	43.50	43.50	95.40	95.39	110.00	110.00
Cd 5085	51.90	51.80	113.60	114.80	130.00	130.20
Cd 4799	60.00	60.01	134.54	134.30	150.00	149.50
Cd 4678	64.75	64.13	144.54	144.20	159.00	159.60
Li 4602	68.00	66.99	150.90	151.10	167.00	166.30
Hg 4358	177.30	177.30	191.00	191.00

THE EFFECT OF SUBSTITUENT GROUPS ON THE ROTATORY POWER

Substituent groups arrange themselves in the following polar series:

OH⁻, Cl, Br, I, C₂H₅, CH₃, H₃, COOH, CHO, COCH₃⁺, CN, NO₂⁺.

In Table II the values of $[\alpha]_{5461}^{20}$ in different solvents are given. The values of K, the rotation constant, as above-defined are also given in brackets for the sake of comparison.

TABLE V
Cinchonidine-o-hydroxy benzoate

Solvent	Pyridine	Methyl alcohol	Ethyl alcohol	Chloroform				
Concentration in gm. 100 c.c.	2.00	0.50	0.50	1.00				
Calculated $[\alpha]$	$\frac{6.759}{\lambda^2-0.0764}$ λ_0 0.2764	$\frac{31.78}{\lambda^2-0.0311}$ 0.1764	$\frac{40.58}{\lambda^2-0.0355}$ 0.1884	$\frac{50.18}{\lambda^2-0.0472}$ 0.2173				
Line	Obs. (O)	Cal. (C)	Obs. (O)	Cal. (C)	Obs. (O)	Cal. (C)		
Li 6708	-17.50°	-18.09°	-75.00°	-75.88°	-98.00°	-97.90°	-124.54°	-124.60
Cd 6438	20.00	19.99	82.00	82.88	107.27	107.10	136.36	136.80
Li 6104	22.75	22.83	94.00	93.09	121.80	120.40	154.00	154.30
Na 5893	25.00	24.96	101.00	100.60	130.00	130.20	166.36	167.30
Hg 5780	26.25	26.23	106.00	104.90	136.40	135.90	175.00	174.90
Hg 5461	30.50	30.48	119.00	119.00	154.50	154.50	200.00	199.90
Cd 5085	37.00	37.08	140.00	139.60	181.80	181.80	237.27	237.20
Cd 4799	43.75	43.78	159.00	159.40	208.18	208.20	272.70	273.80
Cd 4678	47.50	47.43	169.00	169.20	220.90	221.30	292.27	292.20
Li 4602	49.50	49.92	176.00	175.90	230.00	230.20	305.90	304.90
Hg 4358	59.50	59.50	200.00	200.00	262.70	262.60	351.40	351.40

TABLE VI
Cinchonidine benzoate

Solvent	Pyridine	Methyl alcohol	Ethyl alcohol	Chloroform				
Concentration in gm. 100 c.c.	2.00	0.50	0.50	1.00				
Calculated $[\alpha]$	$\frac{8.960}{\lambda^2-0.0744}$ $\lambda_0 0.2728$	$\frac{23.43}{\lambda^2-0.0598}$ 0.2445	$\frac{29.68}{\lambda^2-0.0378}$ 0.1944	$\frac{31.16}{\lambda^2-0.0571}$ 0.2389				
Line	Obs. (O)	Cal. (C)	Obs. (O)	Cal. (C)	Obs. (O)	Cal. (C)		
Li 6708	-25.00°	-23.85°	-60.00°	-60.05	-72.00°	-71.99°	-79.50°	-79.50°
Cd 6438	27.25	26.34	66.37	66.06	79.00	78.79	87.00	87.18
Li 6104	30.00	30.06	75.45	74.92	89.00	88.67	99.00	98.79
Na 5893	32.75	32.92	81.81	81.53	96.00	95.90	107.50	107.40
Hg 5780	34.00	34.49	85.50	85.41	100.00	100.20	112.50	112.50
Hg 5461	40.00	40.04	98.18	98.28	114.00	114.00	129.50	129.20
Cd 5085	48.75	48.62	116.36	117.80	134.00	134.40	154.50	154.50
Cd 4799	57.56	57.44	137.27	137.40	154.00	154.10	178.50	179.90
Cd 4678	62.00	62.00	147.27	147.20	164.00	163.90	192.50	192.60
Li 4602	66.00	65.21	154.50	154.20	170.00	170.60	202.00	201.40
Hg 4358	77.50	77.50	180.00	180.00	195.00	195.00	234.50	234.50

Ortho-substitution.—On comparing the values of $[\alpha]_{5461}^{30}$ and K , it is found that in chloroform, ethyl alcohol and methyl alcohol the order is $H < OH$. This indicates that the introduction of hydroxyl group in place of hydrogen increases the rotation. This does not agree with Rule's polar series.

In pyridine, the order for $[\alpha]_{5461}^{30}$ and K is $OH < H$. This is in conformity with polar series.

Meta-substitution.—On comparing the values of $[\alpha]_{5461}^{30}$ and K , it is found that in ethyl alcohol and methyl alcohol the order is $OH < H$. This again agrees with polar series as the introduction of hydroxyl group in place of hydrogen atom has been found to depress the rotation.

In pyridine the order for $[\alpha]_{5461}^{30}$ and K is $H < OH$, which does not agree with polar series.

Para-substitution.—On comparing the values of $[\alpha]_{5461}^{30}$ and K , it is found that in ethyl alcohol and methyl alcohol, the order is $OH < H$. This again agrees with polar series.

In pyridine the order for $[\alpha]_{5461}^{30}$ and K is $H < OH$, which does not agree with polar series.

SUMMARY

1. The rotatory dispersion of optically active cinchonidine salts of benzoic, *o*-, *m*- and *p*-hydroxy benzoic acids in various non-ionising solvents is found to obey Drude's one term equation $K/\lambda^2 - \lambda_0^2$.
2. The effect of solvents on the rotatory power has also been determined.
3. The effect of position isomerism has been discussed.
4. The influence of introducing the electro-negative hydroxyl group has also been studied.

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2. COHEN, J. B., *Ibid.*, 1903, **83**, 1214 and subsequent papers.

THE NON-LINEAR TORSION OF AN ORTHOTROPIC CYLINDER

BY V. LAKSHMIKANTH AND J. RAMAKANTH

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Received on July 1, 1958

ALTHOUGH the solution of the torsion problems for circular cylinders is known when the twist is very small for several isotropic and anisotropic bodies consisting of single or different materials, it has been noticed to be unsatisfactory when the twist is large, i.e., when the products and squares of the derivatives of displacements can no longer be neglected. For the first time the problem of non-linear torsion of a solid right circular cylinder was solved by B. R. Seth¹ when the material was isotropic and later² when the material had hexagonal type of anisotropy. J. Ramakanth³ solved the problem for a hollow right circular cylinder when the material had hexagonal type of anisotropy and when the material was isotropic. Here the torsion problem for a right circular solid cylinder is solved when the material is orthotropic. We shall make use of the following theorem proved by V. Lakshmikanth⁴ in the course of the proof.

THEOREM: If (i) $h(x, r) \geq 0$ is measurable in x for fixed $r \geq 0$, continuous in r for fixed x ; $x_0 \leq x < \infty$, $r \geq 0$;

(ii) $r(x)$ is the maximum solution of $r' = h(x, r)$ through (x_0, c) where x_0 and c are non-negative constants;

(iii) $y(x)$ is continuous on $x_0 \leq x < \infty$ and satisfies the inequality

$$|\delta y(x)| \leq \int_{x_0}^{x+\delta x} h[s, y(s)] ds, \delta x > 0$$

then

$$y(x) \leq r(x) \quad \text{for } x_0 \leq x < \infty.$$

As an example, numerical values of the constants occurring in the solution are obtained in the case of *Topaz*.

2. THE COMPONENTS OF DISPLACEMENTS, STRAIN AND STRESS

Let a solid right circular cylinder of radius ' a ' whose material is orthotropic be subjected to a finite twist ' T '. From considerations of symmetry it is clear that during torsion cross-sections remain plane and straight radii straight. If the conditions are uniform ' w ' is of the form ' αz ' where α is a constant. The components of displacement may thus be assumed to be given by:

$$u = x(1 - \beta \cos Tz) - y\beta \sin Tz$$

$$v = y(1 - \beta \cos Tz) + x\beta \sin Tz$$

$$w = \alpha z$$

(1)

where α is a constant to be determined and β is a function of the radius r . The strain components are assumed to be given by the equations of the type

$$e_{xx} = \frac{\partial u}{\partial x} - \frac{1}{2} \left[\left(\frac{\partial u}{\partial x} \right)^2 + \left(\frac{\partial v}{\partial x} \right)^2 + \left(\frac{\partial w}{\partial x} \right)^2 \right]$$

$$e_{yz} = \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} - \left[\frac{\partial u}{\partial y} \frac{\partial u}{\partial z} + \frac{\partial v}{\partial y} \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y} \frac{\partial w}{\partial z} \right]$$

and the stress strain relations to be linear.

Substituting the values of u , v , w and transforming into cylindrical co-ordinate system, we obtain:

$$e_{rr} = \frac{1}{2} (1 - \beta^2) - \frac{1}{2} (\beta^2 r^2 + 2r\beta\beta')$$

$$e_{\theta\theta} = \frac{1}{2} (1 - \beta^2)$$

$$e_{zz} = \frac{1}{2} (\epsilon - \beta^2 T^2 r^2)$$

$$e_{\theta z} = Tr\beta^2$$

$$e_{r\theta} = e_{rz} = 0 \quad (2)$$

where

$$\epsilon = 1 - (1 - \alpha)^2.$$

The strain energy function for the orthotropic body is:

$$2W = A e_{rr}^2 + B e_{\theta\theta}^2 + C e_{zz}^2 + 2H e_{rr} e_{\theta\theta} + 2G e_{zz} e_{rr} + 2F e_{zz} e_{\theta\theta} \\ + L e_{\theta z}^2 + M e_{rz}^2 + N e_{r\theta}^2. \quad (3)$$

Hence the non-vanishing components of stress are given by:

$$\widehat{rr} = A (1 - \beta^2 - r^2 \beta^2 - 2r\beta\beta') + H (1 - \beta^2) + G (\epsilon - \beta^2 T^2 r^2)$$

$$2\widehat{\theta\theta} = H (1 - \beta^2 - r^2 \beta^2 - 2r\beta\beta') + B (1 - \beta^2) + F (\epsilon - \beta^2 T^2 r^2)$$

$$2\widehat{zz} = G (1 - \beta^2 - r^2 \beta^2 - 2r\beta\beta') + F (1 - \beta^2) + C (\epsilon - \beta^2 T^2 r^2)$$

$$\widehat{\theta z} = L Tr\beta^2. \quad (4)$$

It is required to determine ϵ and β satisfying the equations of equilibrium and the boundary conditions.

3. SATISFACTION OF THE EQUATIONS OF EQUILIBRIUM

The only equation of equilibrium not identically satisfied is:

$$\frac{\partial}{\partial r} \widehat{rr} + \frac{1}{r} (\widehat{rr} - \widehat{\theta\theta}) = 0 \quad (5)$$

which reduces to

$$8t^2 \beta \beta'' + 8t^2 (\beta')^2 + 4\beta\beta' [(G_1 T^2 + 1) t^2 + 2t + 2] \\ + \beta^2 \{3 + (3G_1 - F_1) T^2 - H_1\} t \\ + 1 - B_1 - (G_1 - F_1) \epsilon = 0 \quad (6)$$

where

$$r^2 = t, \quad G_1 = \frac{G}{A}, \quad F_1 = \frac{F}{A}, \quad H_1 = \frac{H}{A}, \quad B_1 = \frac{B}{A}.$$

Let the solution of the differential equation governing β be:

$$\beta = a_0 + a_1 t + a_2 t^2 + \dots \quad (7)$$

Then we have

$$8a_0 a_1 = 1 - B_1 + (G_1 - F_1) \epsilon - (1 - B_1) a_0^2, \text{ etc.}, \quad (8)$$

' a_n ' being a function of a for $n \geq 1$. The infinite series will define a solution of the equation if it is convergent.

4. CONVERGENCE OF THE SOLUTION

The differential equation (6) may be written as:

$$8t^2 \beta \beta'' + 8t^2 (\beta')^2 + 4\beta \beta' k_1(t) + \beta^2 k_2(t) - k_3 = 0 \quad (9)$$

where

$$k_1(t) = (G_1 T^2 + 1) t^2 + 2t + 2$$

$$k_2(t) = [3 + (3G_1 - F_1) T - H_1] t + 1 - B_1$$

$$k_3 = 1 - B_1 + (G_1 - F_1) \epsilon.$$

Dividing (9) by β^2 and putting $\beta' = \beta Q$, we get:

$$8t^2 Q' + 16t^2 Q^2 + 4k_1(t) Q + k_2(t) - k_3 e^{-\int Q dt} = 0$$

or

$$\begin{aligned} Q' &= 2Q^2 + \frac{1}{t^2} \left(2 + 1_4 + \frac{1_3}{8} e^{-\int Q dt} \right) + \frac{1}{t} \left(2 + \frac{1_2}{8} \right) + \frac{1_1}{2} \\ &= f(t, Q) \text{ say} \end{aligned} \quad (10)$$

where

$$k_1(t) = 1_1 t^2 + 2t + 2$$

$$k_2(t) = 1_2 t + 1_4 \quad (11)$$

$$k_3 = 1_3.$$

Let us consider the region $0 < t \leq 1, 1 \leq Q \leq c$

where c is a constant. $f(t, Q)$ is continuous in the region.

Also

$$|f(t, Q)| \leq \frac{kQ}{t^2} = g(t, Q) \text{ say}$$

where

$$k = 2c_1^2 + \left| 2 + \frac{1_2}{8} \right| + \left| \frac{1_1}{2} \right| + c_2$$

and

$$\left| 2 + \frac{1_4}{8} + \frac{1_3}{8} e^{-c_1 t} \right| \leq c_2.$$

Now $g(t, Q)$ satisfies the conditions of the theorem in 1 in the region under consideration. The solution of the differential equation:

$$Q' = \frac{kQ}{t^2} \text{ is } Q = ce^{-k/t} = R(t) \text{ say}$$

where c is an arbitrary constant.

If $v(t)$ is a solution of $Q' = f(t, Q)$ in power series then

$$v(t) = v(t_0) + \int_{t_0}^t f[t, v(t)] dt.$$

It then follows that

$$|\delta v(t)| \leq \int_t^{t+\delta t} g[t, v(t)] dt.$$

Hence the application of the theorem gives:

$$|v(t)| \leq R(t) \text{ for } t_0 \leq t < 1.$$

$R(t)$ is analytic in the region. Hence $v(t)$ is a bounded function and therefore corresponding power series converges in the region. By going through the substitutions in the reverse order we obtain the solution in power series of (6) which will also be convergent, for $t_0 \leq t \leq 1$.

5. SATISFACTION OF BOUNDARY CONDITIONS

The problem now reduces to finding out the approximate values of a_0 and α satisfying the boundary conditions. They require that:

(i) The boundary $r = a$ should be free from tractions. It is satisfied if $\widehat{rr} = 0$ on $r = a$.

(ii) The tractions on any cross-section should be statistically equivalent to a single couple whose axis is the axis of z . It is satisfied if $\int_0^a r \widehat{zz} dr = 0$.

6. EVALUATION OF CONSTANTS

Because of the complicated nature in which a_0 occurs in a_n for increasing values of n , we shall have to choose a finite number of terms of β series for the

evaluation of constants depending on the degree of accuracy desired. Taking $\beta = a_0 + a_1 t$, the boundary condition reduced to:

$$a^2 [1 + H_1 + a^2 (1 + G_1 T^2)] + 2a_0 a_1 a^2 [3 + H_1 + a^2 (1 + G_1 T^2)] + a_1^2 a^4 [5 + H_1 + a^2 (1 + G_1 T^2)] = 1 + H_1 + G_1 \epsilon \quad (12)$$

$$a_0^2 \left[\frac{a^3}{4} (G + CT^2) + G + F \right] + 2a_0 a_1 a^3 \left[\frac{1}{4} (3G + F) + \frac{a^2}{6} (G + CT^2) \right] + a_1^2 a^4 \left[\frac{4G}{5} + \frac{a}{6} (G + F) \right] + \frac{a^3}{8} (G + CT^2) = G + F + C\epsilon. \quad (13)$$

In the above equations the value of a_1 may be substituted from (8) and the resulting equations be solved as a pair of simultaneous equations for ϵ and a_0 or the three may be considered together to define a_0 , a_1 and ϵ . Substituting for ϵ from (8) in (12) and (13) we obtain:

$$\begin{aligned} k_{10} a_0^2 + k_{11} a_0 a_1 + k_{12} a_1^2 &= k_1 \\ k_{20} a_0^2 + k_{21} a_0 a_1 + k_{22} a_1^2 &= k_2 \end{aligned} \quad (14)$$

where

$$\begin{aligned} k_{10} &= (G_1 - F_1) [1 + H_1 + a^2 (1 + G_1 T^2)] - G_1 (1 - B_1) \\ k_{11} &= 2 (G_1 - F_1) a^2 [3 + H_1 + a^2 (1 + G_1 T^2)] - 8G_1 \\ k_{12} &= (G_1 - F_1) a^4 [5 + H_1 + a^2 (1 + G_1 T^2)] \\ k_1 &= (G_1 - F_1) (1 + H_1) - G_1 (1 - B_1) \\ k_{20} &= (G_1 - F_1) \left[\frac{a^3}{4} (G + CT^2) + (G + F) \right] - C (1 - B_1) \\ k_{21} &= 2 (G_1 - F_1) a^3 \left[\frac{3G + F}{4} + \frac{a^2}{6} (G + CT^2) \right] - 8C \\ k_{22} &= (G_1 - F_1) a^4 \left[\frac{4G}{5} + \frac{a}{6} (G + F) + \frac{a^3}{8} (G + CT^2) \right] \\ k_2 &= (G_1 - F_1) (G + F) - C (1 - B_1). \end{aligned} \quad (15)$$

From the equation (14) we obtain

$$p^2 + k'p + k'' = 0 \quad (16)$$

where

$$\begin{aligned} k' (k_{12} k_2 - k_{22} k_1) &= (k_{11} k_2 - k_{21} k_1) \\ k'' (k_{12} k_2 - k_{22} k_1) &= (k_{10} k_2 - k_{20} k_1) \end{aligned}$$

p gives in general two values. Then since (17)

$$a_0 = \left(\frac{k}{k_{10} + k_{11}p + k_{12}p^2} \right)^{\frac{1}{2}}, \quad (18)$$

the values of a_0 and a_1 can be obtained for each value of p . The correct values of p are those that make $\epsilon < 1$.

The torsional couple N is given by

$$N = 2\pi LT \int_0^a \beta^2 r^3 dr \quad (19)$$

$$= 2\pi LT \left(\frac{a_0^2 a^4}{4} + \frac{a_0 a_1 a^6}{3} + \frac{a_1^2 a^8}{8} \right) \text{ in this case.}$$

Numerical values of a_0 , ϵ and N are obtained for *Topaz* whose elastic constants are given by:

$$\begin{array}{lll} A = 2870 & F = 900 & L = 1100 \\ B = 3560 & G = 860 & M = 1350 \\ C = 3000 & H = 1280 & N = 1330 \end{array}$$

Table for Topaz

Radius	T = 0.1			T = 0.15		
	a_0	ϵ	N	a_0	ϵ	N
$a = 0.5$	0.0480	-0.6643	0.2764	0.0148	-0.3571	3.1098
$a = 0.75$	0.0336	-0.5786	6.2196	0.0333	-0.5714	80.8544
$a = 1.00$	0.0578	+0.1928	39.1142	0.0611	-1.5357	215.6120

Radius	T = 0.20		
	a_0	ϵ	N
$a = 0.50$	0.4745	-3.6500	48.3745
$a = 0.75$	1.0172	+0.4000	113.2600
$a = 1.00$	0.0591	+0.0286	297.1600

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KINETICS OF THE Cu^{++} CATALYSED REACTION BETWEEN H_2O_2 AND $\text{K}_2\text{S}_2\text{O}_8$

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ABSTRACT

The kinetics of the Cu^{++} catalysed reaction between H_2O_2 and $\text{S}_2\text{O}_8^{--}$ has been investigated and the following conclusions have been arrived at as a result of this study.

(1) The total order of the Cu^{++} catalysed reaction between H_2O_2 and $\text{S}_2\text{O}_8^{--}$ is unity. It is unimolecular with respect to $\text{S}_2\text{O}_8^{--}$ and Cu^{++} and zero molecular with respect to H_2O_2 . Since the concentration of catalyst CuSO_4 remains constant throughout the course of reaction, the total order will be unity.

(2) The reaction has a negative salt effect and the nature of this salt effect is a primary exponential one.

(3) The addition of KCl instead of decreasing the rate of reaction in accordance with the general strong inhibitory effect of halide ions observed in most of the $\text{S}_2\text{O}_8^{--}$ reactions, increases the rate of the reaction. This is attributed to the possibility of the formation of some complex between KCl and CuSO_4 which is responsible for decomposing H_2O_2 by itself, thereby showing an apparent increase in the rate of reaction.

Taking into consideration, the general features of $\text{S}_2\text{O}_8^{--}$ reactions and, on the basis of our results, we have proposed a general mechanism for the Cu^{++} catalysed reaction between H_2O_2 and $\text{K}_2\text{S}_2\text{O}_8$.

INTRODUCTION

THE study of the kinetics of oxidation of several reducing agents such as iodide ion, manganous,² thiosulphate,³ oxalate,⁴⁻⁶ chromate,⁷ vanadyl ion,⁸ ammonium,⁹ ammonia¹⁰ and formate ion by $\text{S}_2\text{O}_8^{--}$ by different workers has established the fact that all reactions involving $\text{S}_2\text{O}_8^{--}$ have certain common features, e.g., most of such reactions are unimolecular with respect to $\text{S}_2\text{O}_8^{--}$ and zero molecular with respect to the reducing agent and that they are greatly catalysed by Ag^+ and Cu^{++} ions.

Recently, Srivastava and Ghosh¹²⁻¹³ have investigated the Ag^+ catalysed reaction between H_2O_2 and $\text{K}_2\text{S}_2\text{O}_8$ and have proposed a mechanism for the Ag^+ catalysed reaction. They also found that Cu^{++} catalyses this reaction but a detailed study of the Cu^{++} catalysed reaction was not done by them and hence they have not suggested any mechanism for the Cu^{++} catalysed reaction. It may be mentioned that Cu^{++} catalysed reactions of $\text{S}_2\text{O}_8^{--}$ have not received much attention so far. Allen¹⁴ has, however, recently made a study of the Cu^{++} catalysed oxidation of oxalate ion by $\text{S}_2\text{O}_8^{--}$ and has tried to account for the great

catalytic activity of Cu^{++} on this reaction by supposing the formation of a copper oxalate complex and its subsequent oxidation in the intermediate stages of the reaction. As is clear from the mechanism suggested by Allen, this mechanism cannot be tenable in other copper catalysed reactions of $\text{S}_2\text{O}_8^{--}$. We have, therefore, carried out a detailed study of the Cu^{++} catalysed reaction between $\text{S}_2\text{O}_8^{--}$ and H_2O_2 and, as a result of this study, have suggested a mechanism for this reaction.

During the course of this study we have also observed that a mixture of KCl and CuSO_4 decomposes H_2O_2 .

EXPERIMENTAL

The experimental technique and procedure adopted by us is similar to that followed by Srivastava and Ghosh in the study of this reaction. All the reagents used were either of A.R.B.D.H. or G.R.E. Merck quality. The entire study has been carried out in the dark in order to eliminate the photochemical irregularities.

RESULTS OF THE MEASUREMENTS

First of all the reaction was carried out in the absence of any catalyst in order to compare the catalytic effect of Cu^{++} ion. It was found that in the absence of any catalyst the reaction at 35°C . is very slow, only about $\frac{1}{4}$ fraction decomposing in seven hours time. Therefore, in the next experiment the reaction was performed in the presence of small amount (0.008 M) of CuSO_4 as catalyst. The results of which are recorded in Table I.

TABLE I

($\text{K}_2\text{S}_2\text{O}_8 = 0.01\text{ M}$; $\text{H}_2\text{O}_2 = 0.02\text{ M}$; $\text{CuSO}_4 = 0.008\text{ M}$; Temperature = 35°C .)

Time in minutes	Volume of N/50 potassium permanganate in c.c.	K unimolecular
5	8.72	
10	8.40	0.007462
20	8.18	0.004263
35	7.96	0.003040
50	7.66	0.002981
70	7.20	0.002948
100	6.86	0.002526
130	6.42	0.002450
170	5.98	0.002286
210	5.52	0.002329
	Mean	0.002637

The data in Table I show that the unimolecular constant K is fairly constant after about 20 minutes of the start of the reaction. This shows that the overall reaction is probably unimolecular. The value of the unimolecular constant only slightly decreases with time (*cf.* the decrease in unimolecular constant in this reaction observed by Srivastava and Ghosh). This suggests that probably the concentration of the catalyst goes down with time due to some secondary reaction between CuSO_4 and H_2O_2 , because we have found that CuSO_4 also decomposes H_2O_2 rather slightly.

Temperature coefficient.—The reaction was carried out at 45°C. in order to determine the temperature coefficient and energy of activation of the copper catalysed reaction.

TABLE II

($\text{K}_2\text{S}_2\text{O}_8 = 0.01\text{ M}$; $\text{H}_2\text{O}_2 = 0.02\text{ M}$; $\text{CuSO}_4 = 0.008\text{ M}$; Temperature = 45°C.)

Time in minutes	Volume of N/50 Potassium permanganate in c.c.	K unimolecular
2	8.44	..
10	8.02	0.006383
20	7.14	0.009442
35	6.14	0.009638
50	5.56	0.008694
70	5.26	0.006950
100	4.98	0.005384
	Mean	0.007748

From Table II the temperature coefficient for 10°C. works out to be 2.938 and energy of activation 20,970 gm.—Cals. The comparison of these values with those obtained by Srivastava and Ghosh for the Ag^+ catalysed reaction shows that the Cu^{++} catalysed reaction has a higher temperature coefficient and a higher energy of activation.

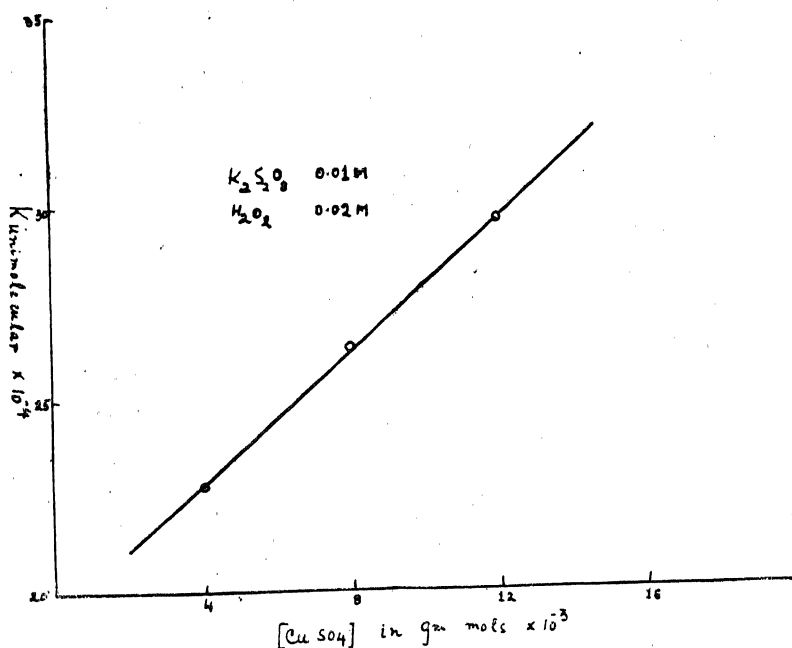
Effect of CuSO_4 concentration.—In order to decide the relationship between CuSO_4 concentration and the rate, the reaction was carried out in presence of different amounts of CuSO_4 as catalyst, the results of which are summarised in Table III.

TABLE III

($\text{K}_2\text{S}_2\text{O}_8 = 0.01 \text{ M}$; $\text{H}_2\text{O}_2 = 0.02 \text{ M}$; Temperature = 35°C .)

Concentration of CuSO_4	Mean value of K unimolecular
0.004 M	0.002271
0.008 M	0.002637
0.012 M	0.002975

This shows that the reaction rate increases only slightly with increase in CuSO_4 concentration. These values of K unimolecular when plotted against the concentration of CuSO_4 give a straight line (Fig. 1) which shows that the rate of reaction is proportional to the first power of Cu^{++} concentration.

FIG. 1. Effect of Cu^{++} Concentration.

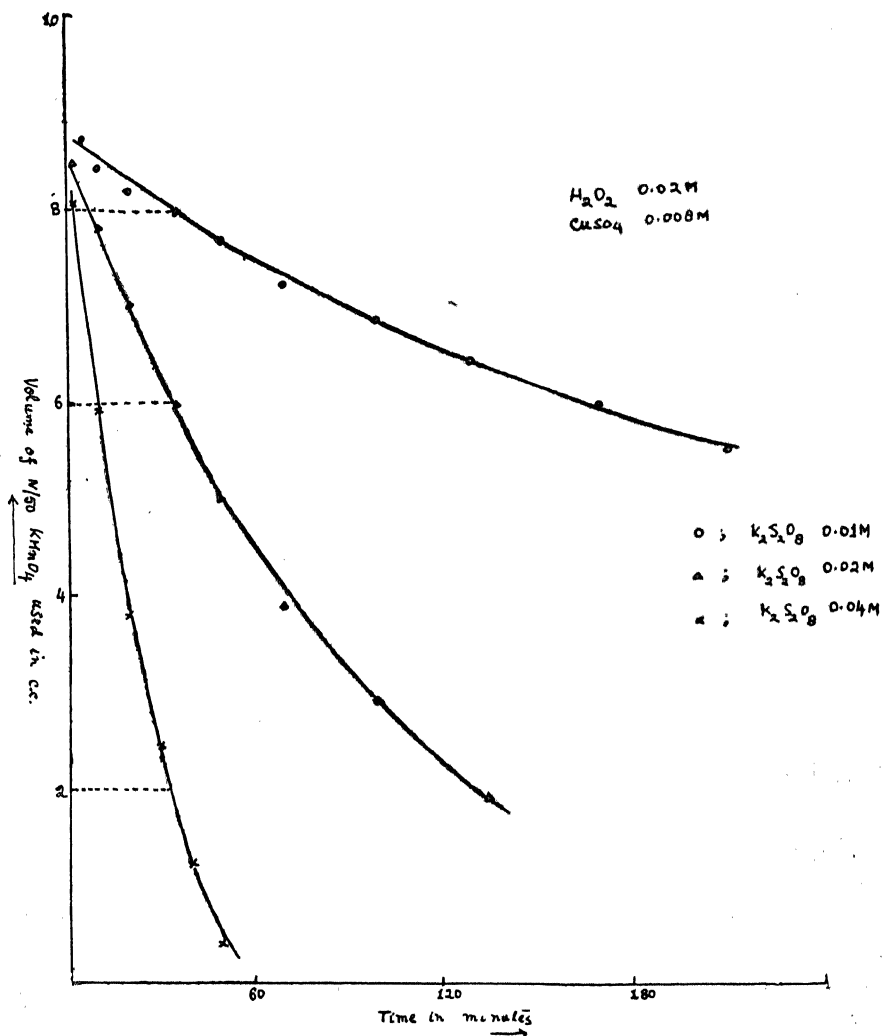
Effect of H_2O_2 concentration.—The reaction was carried out at different initial concentrations of H_2O_2 in order to decide the relationship between H_2O_2 concentration and the rate. Table IV summarises the results of these two measurements.

TABLE IV

(K₂S₂O₈ = 0.01 M; CuSO₄ = 0.008 M; Temperature = 35° C.)

Concentration of H ₂ O ₂	Mean value of K unimolecular
0.02 M	0.002637
0.04 M	0.002663

Therefore, the rate almost remains constant on doubling the concentration of H₂O₂ which shows that the rate determining process for the Cu⁺⁺ catalysed reaction is independent of H₂O₂ concentration.

FIG. 2. Effect of K₂S₂O₈ Concentration.

Effect of $\text{K}_2\text{S}_2\text{O}_8$ concentration.—In order to determine the effect of $\text{K}_2\text{S}_2\text{O}_8$ on the rate determining process the reaction was carried out at three different concentrations of $\text{K}_2\text{S}_2\text{O}_8$, the results of which are summarised in Table V.

TABLE V

($\text{H}_2\text{O}_2 = 0.02 \text{ M}$; $\text{CuSO}_4 = 0.008 \text{ M}$; Temperature = 35°C.)

Concentration of $\text{K}_2\text{S}_2\text{O}_8$	Mean value of K unimolecular
0.01 M	0.002637
0.02 M	0.010806
0.04 M	0.046582

Table V shows that an increase in $\text{K}_2\text{S}_2\text{O}_8$ concentration results in an increase in the unimolecular constant, showing the dependence of the rate on $\text{K}_2\text{S}_2\text{O}_8$ concentration. When the titre values corresponding to different initial concentrations of $\text{K}_2\text{S}_2\text{O}_8$ are plotted against time and the time taken for the same fraction (2/5th) of $\text{K}_2\text{S}_2\text{O}_8$ is read out from the curves in Fig. 2, the times come out to be 33.6, 33.6 and 33 minutes which are approximately constant pointing out clearly the unimolecularity of the reaction with respect to $\text{K}_2\text{S}_2\text{O}_8$.

Salt effect.—In order to determine the nature of the salt effect and thereby the nature of the rate determining process the reaction was carried out at different ionic strengths of the medium by adding varying amounts of K_2SO_4 solution in different experiments. The results of these observations are summarised in Table VI.

TABLE VI

($\text{K}_2\text{S}_2\text{O}_8 = 0.02 \text{ M}$; $\text{H}_2\text{O}_2 = 0.02 \text{ M}$; $\text{CuSO}_4 = 0.008 \text{ M}$; Temperature 35°C.)

Concentration of K_2SO_4	μ	$\sqrt{\mu}$	K	log K
0.0	0.092	0.3033	0.010806	-1.9662
0.025 M	0.167	0.4086	0.009862	-2.0060
0.05 M	0.242	0.4919	0.007547	-2.1222
0.075 M	0.317	0.5630	0.006242	-2.2038
0.1 M	0.392	0.6261	0.005576	-2.2536

The results in Table VI clearly point out that the rate of reaction goes down with an increase in the ionic strength of the medium indicating a negative salt effect. In order to find out the nature of this negative salt effect, i.e., whether it is primary linear salt effect or primary exponential salt effect, the values of log K have been plotted against the square root of ionic strength in Fig. 3. The curve thus

obtained is a linear curve leading to the conclusion that the salt effect is negative and of the primary exponential type.

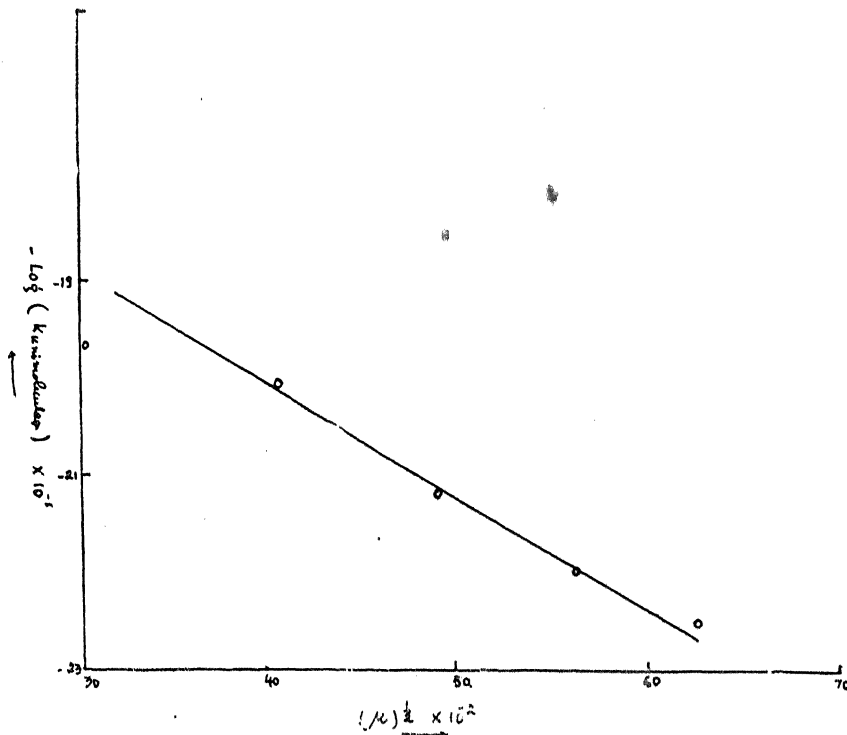


FIG. 3. Nature of salt effect.

Effect of addition of KCl.—Oxidation reactions of $\text{S}_2\text{O}_8^{2-}$ are known to be greatly inhibited by halide ions [cf. the effect of halide ions on $\text{S}_2\text{O}_8^{2-}$ —oxalic acid reaction and $\text{S}_2\text{O}_8^{2-}$ —formate reaction investigated by Srivastava and Ghosh (*loc. cit.*)]. We have, therefore, studied the kinetics of Cu^{++} catalysed reaction in presence of KCl in order to determine the specific effect of halide ions, the results of which are given in Table VII.

A comparison of the data of Table VII with that of Table II shows that the rate constant instead of decreasing, as expected, increases by the addition of KCl. Further it is seen that the k unimolecular goes on decreasing slightly with time.

To find out if H_2O_2 is decomposed by KCl and CuSO_4 mixture at the temperature of the experiment the next experiment was carried out to determine the extent of decomposition of H_2O_2 by KCl- CuSO_4 mixture.

The data in Table VIII show clearly that H_2O_2 is decomposed appreciably by KCl- CuSO_4 mixture and further that this decomposition is also of the first order. Thus it is clear that in the case of the effect of addition of KCl in Cu^{++} catalysed reaction we are really dealing with a case of simultaneous reaction and, therefore, the kinetics of the reactions in this case is not a simple one.

TABLE VII

($K_2S_2O_8 = 0.01$ M; $H_2O_2 = 0.02$ M; $KCl = 0.0053$ M; $CuSO_4 = 0.008$ M
Temperature = 35° C.)

Time in minutes	Volume of N/50 potassium permanganate in c.c.	K unimolecular
2	8.88	..
10	8.48	0.005758
20	8.00	0.005796
35	7.74	0.004166
50	7.34	0.003967
70	6.80	0.003925
100	6.06	0.003899
135	5.60	0.003467

TABLE VIII

($H_2O_2 = 0.02$ M; $KCl = 0.0053$ M; $CuSO_4 = 0.008$ M; Temperature = 35° C.)

Time in minutes	Volume of N/50 potassium permanganate in c.c.	K unimolecular
2	9.94	..
10	9.80	0.001785
20	9.68	0.001471
35	9.46	0.001500
50	9.30	0.001387
70	8.98	0.001494
100	8.76	0.001290
135	8.42	0.001249
170	8.10	0.001219
205	7.80	0.001195
245	7.22	0.001316
	Mean	0.001391

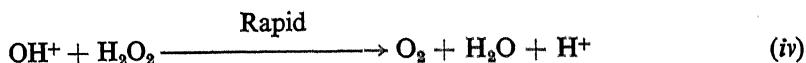
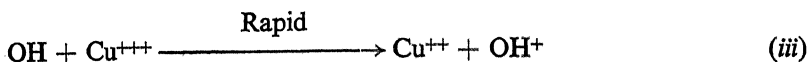
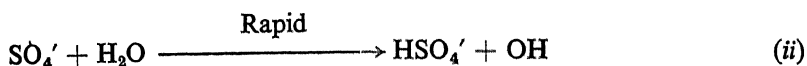
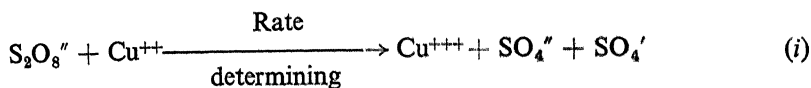
DISCUSSION

Thus we find that the total order of the Cu^{++} catalysed reaction between H_2O_2 and $\text{K}_2\text{S}_2\text{O}_8$ is unity. It is unimolecular with respect to $\text{S}_2\text{O}_8^{--}$ and Cu^{++} ions and zero molecular with respect to H_2O_2 . Therefore, the rate of the reaction will be given by

$$-\frac{dc}{dt} = k \times C_{\text{S}_2\text{O}_8^{--}} \times C_{\text{Cu}^{++}}.$$

The reaction has a negative salt effect and the nature of the salt effect is a primary exponential one.

As pointed earlier, Srivastava and Ghosh, as a result of the study of the kinetics of the Ag^+ catalysed reaction between H_2O_2 and $\text{S}_2\text{O}_8^{--}$ have proposed a general mechanism for the Ag^+ catalysed reaction of $\text{S}_2\text{O}_8^{--}$. Since the Cu^{++} catalysed reaction, as studied by us, follows a similar general behaviour as the Ag^+ catalysed reaction between H_2O_2 and $\text{S}_2\text{O}_8^{--}$ we think that a similar mechanism must hold good for the Cu^{++} catalysed reaction. Taking into consideration these observations we propose the following mechanism for the Cu^{++} catalysed reaction:



The above mechanism proposed is on the lines of the one proposed by Srivastava and Ghosh for Ag^+ catalysed reaction. The rate determining process is between $\text{S}_2\text{O}_8^{--}$ and the catalyst Cu^{++} . Therefore, the rate of the reaction will be given by:

$$-\frac{dc}{dt} = kC_{\text{S}_2\text{O}_8^{--}} \times C_{\text{Cu}^{++}}.$$

If the concentration of Cu^{++} ion during the course of the reaction remains constant, the equation can be written as:

$$-\frac{dc}{dt} = KC_{\text{S}_2\text{O}_8^{--}}$$

and thus the overall rate of reaction should be unimolecular with respect to each of $\text{S}_2\text{O}_8^{--}$ and Cu^{++} ion which is according to our experimental observations.

Since, according to the above mechanism proposed by us, the rate determining process is between two oppositely charged ions hence a negative primary exponential salt effect is accounted for.

The slight decrease of the unimolecular constant with time as observed by us may be due to the secondary reaction of Cu^{++} ion with H_2O_2 and other intermediate species as a result of which the concentration of Cu^{++} ions may not remain constant throughout the course of the reaction and hence the reaction may tend to approach a bimolecular behaviour.

ACKNOWLEDGEMENT

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FORMATION OF PEPTIDE BONDS IN AQUEOUS SOLUTION AND AQUEOUS LINE OF MOLECULAR EVOLUTION

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THE origin of life on earth has drawn the attention of scientists all over the world recently and the symposium on the topic held at Moscow¹ has cleared one thing beyond doubt that life did not originate spontaneously but by a series of chemical evolutions in which preliminary organic compounds, synthesised on the earth by the physico-chemical agencies, formed the basic material for the formation of protoplasm, and the protoplasm itself starting from some primordial material constituting proteins, nucleic acids and adenosine phosphates like non-living material, was capable of adaptation, duplication and self-energy-release-mechanism.

The formation of the preliminary compounds has been studied and in this paper the formation of protein-like compounds having peptide linkages will chiefly be dealt with. The formation of the smallest unit of proteins, *i.e.*, amino acids has been reported in previous communications elsewhere.²⁻⁵

Miller⁶ has observed the formation of several amino acids when a mixture of methane, ammonia, hydrogen and water is exposed to electric discharge. These conditions, according to him, resemble or are similar to the conditions of the earth long before the first living unit appeared on its surface. It is quite probable that the compounds formed in the period when the physico-chemical conditions of the earth were different from what it is at present, might have been the preliminaries of the life which originated afterwards. But our observations have proved that even the present physico-chemical conditions on the earth surface and atmosphere are quite suitable for the formation of amino acids⁷ and if unattacked by the micro-organisms as they were when the life had not originated, amino acids can be synthesised in good quantity from aqueous solutions of organic compounds and nitrate in presence of suitable catalysts and even in aqueous solution of *para*-formaldehyde in presence of colloidal molybdenum oxide as catalyst merely by the irradiation with light.

The formation of peptide linkages from amino acids has been studied by Fox and co-workers.⁸⁻⁹ The reaction $R-CH(NH_2).COOH + H.NH.CHR.COOH \rightarrow RCH(NH_2).CO.NH.CHR.COOH$ is an endothermic one and about 2000-4000 cal. of energy are required to accomplish it, depending on the amino acids forming these peptide linkages.

Fox and co-workers have achieved the synthesis of several peptides by heating amino acids mixture to temperature ranging between 150° and 250° C. The great energy requirement in the peptide formation gives the first impression that the formation of peptides in aqueous solutions will not be possible. However certain peptides have been successfully synthesised in aqueous solutions by exposing

the aqueous solution of amino acids containing some energy-material as sugar, to sunlight.

It was observed that if the above mixture is kept in quartz flask and after sterilization is exposed to sunlight a few peptides are formed in the solution. Similar solution kept in dark did not show the formation of any peptide linkage. A similar solution kept in 'Sigcol' flask indicated only the formation of a single peptide in traces.

To achieve this synthesis an aqueous solution containing 2% of sucrose and 0.1% of glycine was prepared using extra pure chemicals. The pH value of the solution was found to be 6.5. 100 c.c. of this solution was taken out in three 250 c.c. flat-bottom sigcol flasks and in one 250 c.c. quartz flask. The flasks were plugged with surgical cotton and the solutions sterilised at 15 lb. steam pressure for 30 minutes, incubated at 35° C. for 24 hours and again sterilised at 15 lb. pressure for 30 minutes.

One of the above sigcol flasks was thoroughly covered with four folds of thick black cloth from top to bottom and securely tied with the cloth so that no light could pass through it. The second sigcol flask was kept exposed and the third sigcol flask was opened and examined to be sure that in the solution amino acid remains unchanged and no peptide was present in the solution as an impurity. This solution however showed that some of the sucrose was hydrolysed into reducing sugars. This hydrolysis occurred during the sterilisation and the mild acidity of glycine was responsible for this hydrolysis.

The black cloth covered sigcol flask, the second sigcol flask and the quartz flask were exposed to brilliant sunlight for one month. Seven hours exposure was given every day and in the night the flasks were kept in shade. Water temperature in the night was 15° C. but similarly exposed water acquired 35° C. in the noon.

After the exposure the solutions were examined and were found to remain uninfected. The chemical examination of the solutions by partition-paper-chromatographic method employing butanol-acetic acid water mixture as running solvent¹⁰⁻¹¹ and ninhydrin dissolved in acetone as colour producing reagent¹² and burette tests gave the following results. The peptides gave a violet colour only after heating for 20 minutes. The identification of the peptides by paper chromatographic method was done by their R_F values and also by their hydrolysis and subsequent examination on a new paper chromatogram. By comparing the spots obtained from the hydrolysis of the peptides with those obtained from the hydrolysis after deamination of the peptide with nitrous acid, the structure of the dipeptide was established.

Though no quantitative estimation of the peptides formed could be done, the quantity of glycylglycine in uncovered sigcol flask as observed by the intensity of blue colour it produces in burette test showed to be more than what was formed in quartz flask. Quartz flask showed the formation of an appreciable quantity of glycylalanine and glycylnorleucine. The quantity of glycylglycine in the quartz flask was however less than in uncovered sigcol flask.

In this synthesis of peptides the energy required for the formation of peptide bonds came partly by the photodecomposition of water into oxygen and protons and electrons by photons ($nh\nu$) from the sunlight.

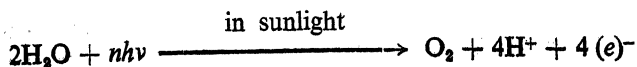


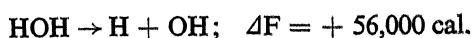
TABLE I

Indicating the formation of peptides in aqueous solutions

Nature of the irradiated solution	Amino acids and peptides detected in the solution
Solution kept in sigcol flask covered with black flask	Glycine
Solution kept in uncovered sigcol flask	Glycine, Glycylglycine
Solution kept in quartz flask	Glycylalanine, glycylnorleucine, Glycylglycine, Glycine, Norleucine.

The $(e)^-$ of this reaction are electrons with high potential energy which is stored in the form of electron-pair bonds. Normally this requires chlorophyll as photocatalyst but it may take place slowly even in the absence of the catalyst. However, some of the various metallic ions present in water in nature may be able to act as photocatalyst for this reaction. The energy thus set free has affected the formation of glycylglycine in the uncovered sigcol flask. There is however another source for the energy required for the formation of peptide bonds in this flask. The energy set free by the light by photodecomposition of water and the oxygen thus formed may oxidise the organic material, present in the solution and sets free more energy and the energy thus liberated will be sufficient to effect peptide formation.

The ultra-violet light ($\lambda < 3200 \text{ \AA}$) has sufficient energy even to break a molecule of water directly into two radicals, one a reductant H and another an oxidant OH which requires 56,000 cal. ($\Delta F = + 56,000 \text{ cal.}$) of energy.



Thus it shall not be difficult for these radiations to provide about 2,500 to 4,000 cal. of energy for the formation of peptide bonds. Positive tests of formation of peptides in the quartz flask indicate that such reactions are taking place.

Absence of any peptide in the solution kept in the covered flask indicates that light and ultra-violet light are capable of synthesising peptide linkages.

Formation of norleucine in free form and as glycylnorleucine in the quartz flask, took place from the six carbon atom chains of hexoses formed by the hydrolysis of sucrose. Their terminal carbon became carboxyl group and the adjacent carbon atom acquired an amino group by the process of transamination from amino group of glycine. The rest of the hydroxy group of the hexose skeleton were replaced by hydrogen atom in the presence of ultra-violet light.

Alanine fraction of glycylalanine is formed by the photolysis of glycine in the presence of ultra-violet light.

The formation of enzymoids has been observed by Gurwitsch¹³ in aqueous solutions of glycine by irradiation. These enzymoids have peptide linkages which are formed during irradiation.

The great similarity of protein molecules¹⁴ indicates either that the molecular evolution is slow or that the origin of the present native proteins are of recent date and it started when the physico-chemical condition of the earth was very similar to that of the present day. The change of environment is responsible for the progress of evolution. In case of molecular evolution this change of environment affecting the evolution will be only the changes in the physico-chemical conditions of the earth. As these changes are extremely slow and very little changes in the physico-chemical conditions of the earth has taken place from the time of the origin of proteins to the present age, only a little change in the nature of protein molecules has taken place.

Formation of amino acids and peptides in aqueous solution and the similarity of protein molecules indicate that molecular evolution leading to the formation of proteins, the chief ingredient of the preliminary protoplasm, originated when the physico-chemical conditions of the atmosphere and surface of the earth became very similar to what it is at present and is thus of fairly recent origin.

SUMMARY

An aqueous solution of glycine and sucrose, when exposed to visible and ultra-violet light of sunlight under sterilised conditions for about 200 hours, indicates the formation of peptides. The solution which was irradiated in sigcol flask and thus allowed exposure to only visible light indicated the formation of glycylglycine but the solution kept in the quartz flask and thus exposed to ultra-violet radiations also, indicated the formation of glycylalanine, glycylnorleucine, and glycylglycine. A similar solution kept covered with black cloth did not indicate the formation of any peptide.

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A STUDY OF THE INFLUENCE OF THE CHANGE OF CARBON-NITROGEN RATIO ON THE LOSS OF NITROGEN AND OTHER PHYSIOLOGICAL PROPERTIES OF *PICHIA INDICA* IN CULTURES CONTAINING UREA AND ETHYL ALCOHOL AS SOURCES OF NITROGEN AND CARBON UNDER NON-AERATED CONDITION

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INTRODUCTION

WHEN ammonium sulphate is used as the source of nitrogen in soil about 50 per cent. of its nitrogen is lost. Dhar and Pant¹ have observed considerable loss of nitrogen during the process of active nitrification of ammonium salts or other nitrogenous compounds in soil. In the case of soil this loss is attributed to the simultaneous presence of ammonium and nitrite ions and eventual liberation of free nitrogen. There are several references where plants also show loss of molecular nitrogen in some stage of their growth. Pearsall and Billimoria² in their work on *Narcissus narcissus* leaves and Vickery in his work³ on *Narcissus peticus* leaves mention loss of nitrogen in developing leaves. This they attribute to the oxidation of ammonia from deamination of amino acids to nitrite.

Though yeast cannot live in cultures containing nitrite ions, a considerable loss of fixed nitrogen has been observed in the cultures of *Pichia indica*⁴ under different conditions of culture composition.⁵⁻⁹

Here in this paper the loss of nitrogen in cultures of *Pichia indica* containing urea as the source of nitrogen has been investigated. *Pichia indica* can utilise ethyl alcohol as the source of carbon.¹⁰ Ethyl alcohol was used as the source of carbon food of the yeast for this study.

EXPERIMENTAL

Three cultures each containing 0.1 g. of calcium carbonate, 0.1 g. of disodium hydrogen phosphate, 0.1 g. of sodium chloride, 0.1 g. of potassium sulphate, 0.025 g. of zinc sulphate and 0.125 g. of magnesium sulphate were prepared. These minerals were weighed in 500 c.c. flat bottom pyrex flasks and to them urea as mentioned was added. 50 c.c. of distilled water were added in the flask and minerals were digested in dilute hydrochloric acid. Total volume of the medium was made to 200 c.c. and pH adjusted to 4.5.

The flasks were plugged with surgical cotton and the media sterilised at 15 lb. pressure for 30 minutes in an autoclave. On cooling, they were seeded with a trace of *Pichia indica*.

The cultures were kept for 50 days for fermentation at room temperature which varied between 18 and 22.5° C. during this period.

The nitrogen of the culture was estimated by standard Kjeldhal and Gunning method.

OBSERVATION

Results obtained by the analysis of the cultures are tabulated in Table I.

TABLE I

Influence of carbon-nitrogen ratio on alkali formation and alcohol consumption

G. of urea added	C/N ratio of culture	G. of ethyl alcohol left	G. of ethyl alcohol consumed	G. of alkali formed	% of alkali formation on the basis of alcohol consumed
3.6736	2.5	1.84	6.20	0.2620	4.22
1.8368	5.0	0.46	7.58	0.1692	2.23
0.9184	10.0	0.42	7.62	0.0554	0.73

TABLE II

Growth of yeast and consumption of nitrogen

C/N ratio of the culture	G. of yeast grown	% of yeast yield	G. of N in the culture in the beginning	G. of N left in the culture	G. of N consumed
2.5	2.6722	43.10	1.7142	1.4983	0.2159
5.0	3.5954	47.43	0.8571	0.7001	0.1570
10.0	3.8498	50.52	0.4285	0.2967	0.1318

DISCUSSION

In *Pichia indica* cultures containing urea as the source of nitrogen and ethyl alcohol as the source of carbon a considerable amount alkaline material is formed whose formation decreases with the increase of carbon-nitrogen ratio of the culture. The percentage yield of yeast calculated on the basis of ethyl alcohol consumed increases with the increase of C/N ratio of the cultures. Between the range of

TABLE III

Percentage loss of nitrogen and nitrogen content of the yeast

C/N ratio of the culture	G. of N in yeast cell	G. of N lost from the culture	% of N lost on the basis of nitrogen consumed	% of N in the yeast
2.5	0.0913	0.0246	57.71	1.48
5.0	0.1229	0.0341	21.72	6.69
10.0	0.1295	0.0023	1.74	14.10

C/N ratio studied the loss of nitrogen rapidly decreases with the increase of C/N ratio of the culture. It is very interesting to observe that the percentage of nitrogen in the yeast cells rapidly increases with the increase of C/N ratio, i.e., decrease of urea concentration in the culture. Thus yeast grown in a culture containing 3.6736 g. of urea has 2.48 per cent. of nitrogen where as if it is grown in cultures containing 0.9184 g. of urea, 14.10 per cent. of nitrogen is present in the yeast cells.

SUMMARY

When *Pichia indica* is grown in cultures containing urea and ethyl alcohol as sources of nitrogen and carbon, the cultures become alkaline due to the formation of certain alkaline material. The yeast yield and percentage of nitrogen in the yeast increases with the increase of C/N ratio of the culture. Percentage of loss of nitrogen from the cultures decreases with the increase of carbon ratio of the culture.

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EFFECT OF THE DILUTION ON THE ELECTRICAL CONDUCTANCE AND pH OF THE HYDROUS FERRIC OXIDE SOLS OF DIFFERENT PARTICLE SIZES

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ABSTRACT

The present paper deals with the study of the effect of dilution on the electrical conductance and pH of the hydrous ferric oxide sols having colloidal micelles of different grain sizes. The results obtained show that with the dilution of hydrous ferric oxide sol there occurs desorption of hydrogen ions from the surface of the colloidal particles, which causes the liberation of chloride ions from the double layer making them osmotically active. These desorbed hydrogen ions and liberated chloride ions increase the specific conductance of the diluted sol, but the decrease in the charge on the surface of the colloidal particles makes their electrical contribution less. It has been shown in this paper that with the dilution of hydrous ferric oxide sol the factor, specific conductance/ $[H^+]$ if plotted against dilution decreases slowly and passes through a minimum point. This minimum point is more prominent in the case of sol possessing smaller colloidal micelles than sol containing bigger colloidal micelles.

It has been shown by us in an earlier paper¹ that the colloidal hydrous ferric oxide tends to behave as colloidal electrolyte when the size of the particles is decreased. The effect of dilution on the electrical conductance and pH of the hydrous ferric oxide sol having different sized particles have been studied. The results here show that with the dilution of the sol there occurs a desorption of hydrogen ions from the surface of the colloidal particles, which also liberates chloride ions from the double layer. This increases the specific conductance of diluted sol, but with decrease in the charge on the colloidal particles, their contribution to electrical conductance also decreases. It is found that with dilution the factor, specific conductance/ $[H^+]$ plotted against the dilution of the sol decreases and passes through a minimum point, then increases and finally again decreases through a maximum. This minimum is more prominent in the case of sol possessing smaller colloidal particles than those consisting of larger ones.

PREPARATION

Hydrous ferric oxide was precipitated from concentrated solution of ferric chloride (B.D.H.) with the addition of an equivalent amount of ammonium hydroxide, at room temperature with constant stirring. The precipitate was washed by decantation till it tended to peptize. This precipitate was then passed through a Sharples Laboratory Supercentrifuge maintained at the speed 20,000 r.p.m. Distilled water was constantly fed and the process was continued till the outcoming liquid was free from chloride. The reddish brown precipitate was then removed

from the bowl, made into a paste with water and poured into a large bulk of water for further washing. It was continued till the supernatant liquid was free from chloride ions. The precipitate of hydrous ferric oxide was peptized by shaking, at a constant rate by a Microid Shaker for about forty-eight hours, with hydrochloric acid (A.R. Quality) of approximately 0.045 N strength. A clear brick-red colloidal solution of hydrous ferric oxide was obtained.

By keeping the Sharple's Laboratory Supercentrifuge at the speeds of 4,000, 9,000, 16,000 and 24,000 r.p.m., four sol samples of different grain sizes were obtained from the same mother sol. Their chloride and iron contents were estimated both gravimetrically and volumetrically. For the purpose of study, all the four samples were adjusted to contain the same amount of iron per litre of the sol, by diluting wherever necessary.

Sols obtained at the speeds 4,000, 9,000, 16,000 and 24,000 r.p.m. were termed A, B, C and D respectively. The iron content, which was made same in all the four sol samples, was 4.44 gm. per litre of the sol. The chloride concentrations in the sol samples A, B, C and D were respectively 0.01976, 0.02004, 0.02060 and 0.02108 gm. ions per litre of the sol.

pH AND CONDUCTIVITY RESULTS

The conductivity and pH measurements were performed with a Leeds and Northrup Kohlrausch bridge with an Audiofrequency Oscillator, and a Cambridge Portable PH Meter respectively. The results obtained with the four sol samples A, B, C and D are given in Tables I, II, III and IV.

The factor, specific conductance/[H⁺] was plotted against the dilution of the sol and curves 1, 2, 3 and 4 (Fig. 1) were obtained. It appears that the curve decreases slowly and passes through a minimum, as shown by the point M, then increases and finally again decreases after passing through a maximum point. This maximum point, M, is more prominent in the case of sol possessing smaller colloidal micelles than one containing bigger ones.

This behaviour is explained from the fact that with progressive dilutions of the sol, more and more hydrogen ions become available in the system, because of their release from the colloidal surface. Subsequent decrease in the charge of the colloidal particles leads to a decrease in their conductance contribution. The perusal of Tables I, II, III and IV shows that the colloidal solution having smaller grain size possesses more peptizing electrolyte, *i.e.*, hydrochloric acid than the sol containing bigger colloidal micelles. Thus the hydrogen ions, imparting electric charge, increase with the decrease in the size of the colloidal grains and it is so because more surface is available for adsorption from smaller sized colloidal particles than from bigger ones. The results presented here clearly show that there is more desorption of hydrogen ions from the surface of the colloidal grains containing smaller particles than one containing bigger colloidal micelles, which is responsible for the more prominent minimum point in the curve, in the case of former sol than in latter one.

From the results obtained, it appears that the decrease in the conductance of the colloidal particles with increasing dilutions is less rapid than the release of the hydrogen ions from the colloidal surface. The release of the hydrogen ions

TABLE I

(Iron = 4.44 gm. per litre of sol; Chloride = 0.01976 gm. ions per litre of sol A; Solution Temperature = 27° C.)								
Dilution of the sol	Specific conductivity in $\text{Mhos} \times 10^3$ (observed)	Specific conductivity in $\text{Mhos} \times 10^3$ (theoretical)	Difference of columns 2 & 3	pH	Hydrogen-ion concentration in gram ions per litre $\times 10^3$ (observed)	Hydrogen-ion concentration in gram ions per litre $\times 10^3$ (theoretical)	Difference of columns 6 & 7	Sp. conductance $\times 10$ [H ⁺]
1	2	3	4	5	6	7	8	9
1.0	2.167	2.58	2.63	8.235
0.9	2.020	1.950	0.070	2.61	3.455	2.367	0.088	8.226
0.8	1.840	1.7336	0.1064	2.65	2.239	2.104	0.135	8.219
0.7	1.672	1.5169	0.1551	2.70	1.995	1.841	0.114	8.381
0.6	1.492	1.3002	0.1918	2.75	1.778	1.578	0.200	8.392
0.5	1.305	1.0835	0.2215	2.81	1.549	1.315	0.234	8.424
0.4	1.096	0.8668	0.2292	2.88	1.318	1.052	0.266	8.320
0.3	0.8835	0.6500	0.2335	2.97	1.072	0.789	0.283	8.245
0.2	0.6503	0.4334	0.2169	3.10	0.7943	0.526	0.2683	8.187
0.1	0.3799	0.2167	0.1632	3.33	0.4677	0.263	0.2047	8.123

TABLE II
(Iron = 4.44 gm. per litre of sol ; Chloride = 0.02004 gm. ions per litre of sol B; Solution Temperature = 27° C.)

Dilution of the sol	Specific conductivity in $\text{Mhos} \times 10^3$ (observed)	Specific conductivity in $\text{Mhos} \times 10^3$ (theoretical)	Difference of columns 2 & 3	pH	Hydrogen-ion concentration in gram ions per litre $\times 10^3$ (observed)	Hydrogen-ion concentration in gram ions per litre $\times 10^3$ (theoretical)	Difference of columns 6 & 7	Sp. conductance $\times 10^4$ $[\text{H}^+]$
1	2	3	4	5	6	7	8	9
1.0	2.191	2.57	2.692	8.139
0.9	2.032	1.9719	0.0601	2.60	2.512	2.423	0.089	8.102
0.8	1.862	1.7528	0.1092	2.63	2.344	2.1536	0.1904	7.943
0.7	1.734	1.5337	0.2003	2.68	2.089	1.8844	0.2046	8.316
0.6	1.511	1.3146	0.1964	2.74	1.820	1.615	0.2050	8.303
0.5	1.346	1.0955	0.2505	2.78	1.660	1.346	0.314	8.286
0.4	1.112	0.8764	0.2356	2.87	1.380	1.0768	0.3132	8.243
0.3	0.8941	0.6573	0.2368	2.96	1.096	0.8076	0.2884	8.155
0.2	0.6557	0.4382	0.2175	3.08	0.8318	0.5384	0.2934	7.883
0.1	0.3815	0.2191	0.1624	3.31	0.4898	0.2692	0.2206	7.789

TABLE III

(Iron = 4.44 gm. per litre of sol; Chloride = 0.02060 gm. ions per litre of sol C; Solution Temperature = 27° C.)

Dilution of the sol	Specific conductivity in Mhos $\times 10^3$ (observed)	Specific conductivity in Mhos $\times 10^3$ (theoretical)	Difference of columns 2 & 3	pH	Hydrogen-ion concentration in gram ions per litre $\times 10^3$ (observed)	Hydrogen-ion concentration in gram ions per litre $\times 10^3$ (theoretical)	Difference of columns 6 & 7	Sp. conduc- tance $\times 10$ [H ⁺]
1	2	3	4	5	6	7	8	9
1.0	2.274	2.50	3.162	0.7188
0.9	2.124	2.046	0.078	2.52	3.020	2.845	0.175	0.7033
0.8	1.966	1.819	0.147	2.54	2.818	2.529	2.89	0.6817
0.7	1.772	1.591	0.181	2.60	2.512	2.213	0.299	0.7055
0.6	1.595	1.364	0.231	2.65	2.239	1.897	0.342	0.7124
0.5	1.396	1.137	0.257	2.71	1.995	1.581	0.414	0.7158
0.4	1.186	0.899	0.287	2.78	1.622	1.264	0.358	0.7145
0.3	0.950	0.682	0.268	2.86	1.380	0.9486	0.4314	0.6882
0.2	0.695	0.455	0.240	3.02	0.955	0.6324	0.3226	0.6637
0.1	0.401	0.227	0.174	3.21	0.537	0.3162	0.2208	0.6513

TABLE IV

(Iron = 4.44 gm. per litre of sol; Chloride = 0.02108 gm. ions per litre of sol D; Solution Temperature = 27°C.)

Dilution of the sol	Specific conductivity in Mhos $\times 10^3$		Specific conductivity in Mhos $\times 10^3$ (theoretical)	Difference of columns 2 & 3	pH	Hydrogen-ion concentration in gram ions per litre $\times 10^3$ (observed)	Hydrogen-ion concentration in gram ions per litre $\times 10^3$ (theoretical)	Difference of columns 6 & 7	Sp. conductance $\times 10$ [H ⁺]
	(observed)								
1	2	3	4	5	6	7	8	9	
1.0	2.311	2.48	3.311	6.977
0.9	2.184	2.080	0.104	2.50	3.162	2.980	0.182	0.182	6.907
0.8	1.919	1.8488	0.0702	2.52	3.020	2.648	0.372	0.372	6.353
0.7	1.823	1.6177	0.2053	2.56	2.754	2.3174	0.4366	0.4366	6.618
0.6	1.633	1.3866	0.2464	2.62	2.399	1.986	0.4130	0.4130	6.810
0.5	1.418	1.1555	0.2625	2.68	2.089	1.655	0.434	0.434	6.787
0.4	1.193	0.9244	0.2686	2.75	1.778	1.324	0.454	0.454	6.705
0.3	0.9672	0.6933	0.2739	2.84	1.445	0.993	0.452	0.452	6.691
0.2	0.7063	0.4632	0.2441	2.97	1.072	0.662	0.410	0.410	6.592
0.1	0.4097	0.2311	0.1786	3.21	0.6168	0.331	0.2858	0.2858	6.492

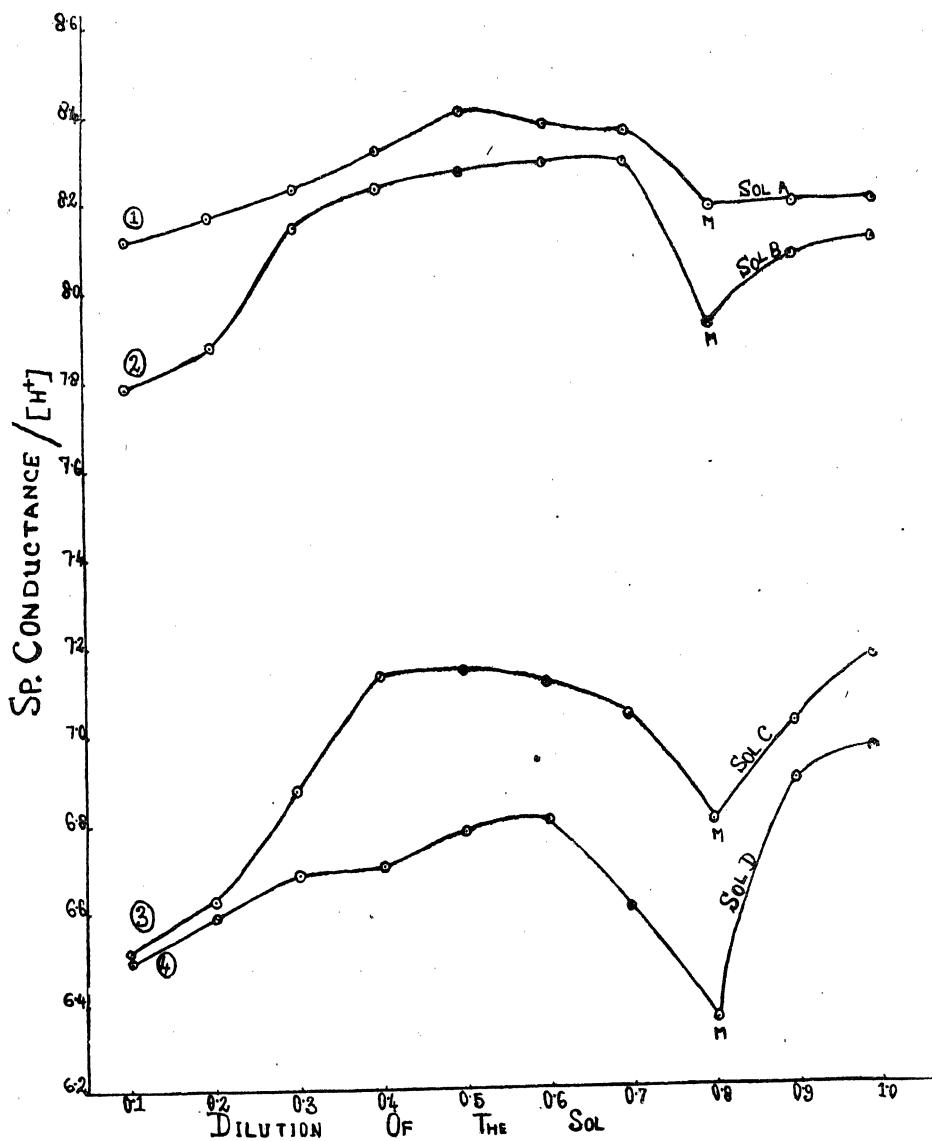


FIG. 1

from the colloidal surface is more rapid in the earlier stages of dilution than afterwards.

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SPECTRUM OF HD 223385

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ABSTRACT

Blue spectrum of the super-giant star HD 223385 has been described and compared with the spectrum of α -Cygni. This spectrum can be classified as one between A2 and A3 in agreement with what is used in previous literature. From the measurements of equivalent width of H_γ the absolute magnitude of -7.1 is derived. The value of Balmer discontinuity is 0.4 which agrees well with that found by Miss Hack. The electron pressure of the order of unity is found from the hydrogen lines by English Teller formula. This electron pressure is less than the one obtained from the curve of growth analysis by a factor of about a hundred. The turbulent velocities of 15 km./sec. and 30 km./sec. are found for small and large eddies respectively from the study of the relation of equivalent widths of the lines with their half-widths and depths.

INTRODUCTION

HD 223385 (6 Cassiopeiæ) is a super-giant star with 'C' characteristic. Its position in the sky is given by $\alpha_{1900} = 23^h 44^m$, $\delta_{1900} = 61^\circ 40'$. In the previous literature the spectrum is sometimes classified as A2p and sometimes A3. Visual apparent magnitude of the star is 5.71 . The distance as derived by Merrill, Sanford, Wilson and Burwell¹⁻² (1937, 1938) from the equivalent widths of D_1 and D_2 lines of sodium, is 3000 parsecs. These lines are mainly interstellar. When this distance is combined with the visual apparent magnitude one finds its absolute magnitude of the order of -9 corrected for interstellar absorption. In the spectrograms taken with high dispersion several components of these lines can be distinguished³ (Münch, 1957). Even on the present plates which are taken with only moderate dispersion two components are quite undoubtedly separated and even a third one is suspected although it is not definitely resolved. From the measurements of the equivalent width of H_γ Petrie and Maunsell⁴ (1950) have derived the spectroscopic absolute magnitude of -7.1 . Anyway there is no doubt that this super-giant is one of the intrinsically brightest stars in the sky. The colour excess has been measured photoelectrically by Stebbins, Huffer and Whitford⁵ (1940) and photographically by O'Keefe⁶ (1941). The values arrived at in the two investigations are $+0.29$ and $+0.34$ respectively.

A rough study of the spectrum of this star has been made by McKellar⁷ (1939) at the Dominion Astrophysical Observatory, Royal Oak. In the spectrum H_α has the characteristic of a P-Cygni type profile. On the basis of this H_α profile Beals⁸ (1951) listed this star as a P-Cygni star of type IV. This P-Cygni type profile of H_α is quite similar to that in the spectrum of α -Cygni, but the emission is considerably more intense in 6 Cas. than in α -Cygni. Besides this, H_α absorption has

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been observed double at times. A separate study of the variations of H_{α} has been made by the author in collaboration with McKellar.⁹

SPECTROGRAMS AND TRACINGS

In the present note the spectrum of 6 Cassiopeiæ in the blue region is described. The plates listed in Table I were taken by McKellar at the Dominion Astrophysical Observatory, Royal Oak, with the Universal Spectrograph at the Cassegranian focus of 72 inch telescope. To get the moderate dispersion, two prisms were used.

TABLE I

Plate No.	Designation	Slit width	Date	J. D.
Å 28973	11 L	0.002	18-12-1938	9251.603
Å 22751	11 M	0.002	12-10-1939	9549.7305
Å 22799	11 L	0.0025	31-10-1939	9568.793

The camera used was of focal-length 96 centimeters for two plates designated as 11 L and 71 centimeters for one plate designated as 11 M. The original dispersions thus obtained for the two types of plates are listed in Table II.

TABLE II

Wave-length	Dispersion in Å/mm.	
	11 L	11 M
3900Å	6.4	8.6
H_{δ}	8.4	11.4
H_{γ}	11.0	14.9
4600Å	14.1	19.2

Every plate carries an intensity calibration which is superimposed on the plates with the aid of a calibration spectrograph mounted in a cupboard on the observing floor. A rotating sector operated at a speed of hundred revolutions per second or an absorbing wedge in contact with the slit provided the necessary gradation of light intensity. The wave-lengths in the calibration spectrum could be determined with the help of a mercury spectrum. The tracings are made with the help of photoelectric recording microphotometer of the Dominion Astrophysical Observatory designed by Beals¹⁰ (1936). This microphotometer changes the blackness of the plate into the deflection of the galvanometer. Finally this

deflection of the galvanometer was changed into the intensity tracing directly with the help of intensitometer constructed by Girling and described by Beals¹¹ (1944) at Royal Oak. On these tracings the identifications of the lines were made with the help of the list of lines in α -Cygni published by Wyse¹² (1938). All the lines thus identified are listed in Table III. In the region described here in the spectrum of the present star all the lines are observed in absorption only.

TABLE III

The blue spectrum of HD 223385

Wave-length	Solar wave-length	Identification	Multiplet	Lower Ext. Pot.	Blending	Contribution to the blend	Intensity
3905.64	3905.66 L	Cr II	167	5.307	B	+	4
3906.037	3906.03	Fe II	173	5.547		+++	
3913.464	3913.47	Ti II	34	1.111	7
3914.333	3914.33	V II	33	1.785	B	++	4
3914.480	3914.51	Fe II	3	1.663		+++	
3916.418	3916.41	V II	10	1.421	1
3922.914	3922.92	Fe I	4	0.051	1
3927.922	3927.94	Fe I	4	0.110	1
3930.299	3930.31	Fe I	4	0.087	B	++	3
3930.31	3930.31 C	Fe II	3	1.688		+++	
3932.007	3932.02	Ti II	34	1.126	2
3933.664	3933.68	Ca II (K)	1	0.000	15
3935.942	3935.98	Fe II	173	5.545	3
3938.289	3938.30	Fe II	3	1.663	B	+++	5
3938.969	3938.97	Fe II	190	5.885		+++	
3945.11	3945.11	Cr II	142	4.923	B	+	2
3945.21	3945.22	Fe II	3	1.688		+++	

TABLE III (Contd.)

Wave-length	Solar wave-length	Identification	Multiplet	Lower Ext. Pot.	Blending	Contribution to the blend	Intensity
3947·301	3947·33 L	O I	3	9·11	B	..	1
3947·489	3947·51 L	O I	3	9·11			
3947·594	3947·61 L	O I	3	9·11			
3951·968	3951·97	V II	10	1·470	1
3964·727	3964·73 L	He I	5	20·53	1
3968·470	3968·49	Ca II (H)	1	0·000	B	+++	20
3970·074	3970·08	H ϵ	1	10·16		+++	25
3973·642	3973·64 L	V II	9	1·421	B	++	4
3974·160	3974·17	Fe II	29	2·693		++	
3979·51	3979·51 L	Cr II	183	5·645	2
3981·61	3981·62	Fe II	3	1·717	B	+++	1
3981·998	3982·00	Ti II	11	0·571		+++	
3997·126	3997·11	V II	9	1·470	B	+++	1
3997·394	3997·40	Fe I	278	2·716		..	
4002·073	4002·08	Fe II	29	2·766	B	+++	4
4002·549	4002·55 L	Fe II	190	5·930		+++	
4005·246	4005·26	Fe I	43	1·551	B	+++	2
4005·712	4005·71	V II	32	1·809		+++	
4009·270	4009·27 L	He I	55	21·13	1
4012·372	4012·39	Ti II	11	0·571	B	+++	4
4012·50	4012·50 L	Cr II	183	5·638		+	
4014·489	4014·53	Sc II	8	0·314	1

TABLE III (Contd.)

Wave-length	Solar wave-length	Identification	Multiplet	Lower Ext. Pot.	Blending	Contribution to the blend	Intensity
4015·50	4015·48	Ni II	12	4·015	2
4023·388	4023·39	V II	32	1·797	1
4024·552	4024·58	Fe II	127	4·475	4
4025·136	4025·14	Ti II	11	0·605	1
4026·189	4026·19 L	He I	18	20·87	B	+++	1
4026·362	4026·36 L	He I	18	20·87		+	
4028·332	4028·35	Ti II	87	1·884	3
4030·755	4030·73 L	Mn I	2	0·000	1
4032·946	4032·97	Fe II	126	4·475	B	++	2
4033·073	4033·08	Mn I	2	0·000		++	
4034·490	4034·49	Mn I	2	0·000	1
4035·631	4035·61	V II	32	1·785	1
4038·03	4038·04 L	Cr II	194	6·459	1
4045·815	4045·83	Fe I	43	1·478	4
4048·831	4048·83 L	Fe II	172	5·545	3
4051·97	4052·03	Cr II	19	3·09	2
4053·45	..	Cr II	19	3·09	B	++++	4
4053·815	4053·83	Ti II	87	1·885			
4054·11	..	Cr II	19	3·09			
4057·505	4057·52	Mg I	16	4·327	1
4063·597	4063·61	Fe I	43	1·551	2
4067·051	4067·04 L	Ni II	11	4·012	4

TABLE III (Contd.)

Wave-length	Solar wave-length	Identification	Multiplet	Lower Ext. Pot.	Blending	Contribution to the blend	Intensity
4069·883	4069·91	Fe II	188	5·885	B	++	1
4070·03	4070·05	Fe II	22	2·533		+++	
4071·740	4071·75	Fe I	43	1·601	2
4077·714	4077·73	Sr II	1	0·000	3
4086·14	4086·13	Cr II	26	3·698	1
4101·737	4101·75	H δ	1	10·16	20
4111·01	4111·00	Cr II	18	3·742	B	+++	2
4111·01	4111·00	Cr II	26	3·090		++	
4113·24	4113·23	Cr II	18	3·093	1
4119·53	4119·53	Fe II	21	2·533	1
4120·812	4120·81 L	He I	16	20·87	B	+++	1
4120·993	4120·98 L	He I	16	20·87		++	
4122·638	4122·67	Fe II	28	2·572	5
4124·793	4124·79	Fe II	22	2·533	2
4128·053	4128·05 L	Si II	3	9·794	B	..	6
4128·735	4128·74	Fe II	27	2·572		..	
4130·884	4130·88 L	Si II	3	9·797	8
4132·060	4132·07	Fe I	43	1·601	B	+++	1
4132·41	4132·41	Cr II	26	3·742		+++	
4138·40	4138·36	Fe II	39	2·816	1
4143·759	4143·77 L	He I	53	21·13	B	++	2
4143·871	4143·88	Fe I	43	1·551		++	

TABLE III (Contd.)

Wave-length	Solar wave-length	Identification	Multiplet	Lower Ext. Pot.	Blending	Contribution to the blend	Intensity
4145·77	4145·77 L	Cr II	162	5·296	2
4161·524	4161·52	Ti II	21	1·079	2
4163·644	4163·66	Ti II	105	2·579	4
4171·897	4171·91	Ti II	105	2·586	4
4173·450	4173·47	Fe II	27	2·572	B	+++	8
4173·537	4173·55	Ti II	21	1·079		+	
4174·088	..	Ti II	105	2·59	2
4177·70	4177·70	Fe II	21	2·533	4
4178·855	4178·86	Fe II	28	2·572	8
4187·044	4187·04	Fe I	152	2·44	B	..	1
4187·802	4187·80	Fe I	152	2·41			
4192·07	4192·02	Ni II	10	4·015	1
4198·310	4198·34	Fe I	152	2·389	1
4202·031	4202·04	Fe I	42	1·478	B	+++	1
4202·350	4202·36	V II	25	1·696		+	
4215·524	4215·54	Sr II	1	0·000	2
4222·219	4222·22	Fe I	152	2·439	1
4224·09	..	Cr II	31	3·84	B	+++	1
4224·51	..	V II	25	1·68		+	
4226·728	4226·74	Ca I	2	0·000	B	+++	1
4227·14	4227·16	Fe II	45	2·879		+	

TABLE III (Contd.)

Wave-length	Solar wave-length	Identification	Multiplet	Lower Ext. Pot.	Blending	Contribution to the blend	Intensity
4233·167	4233·17	Fe II	27	2·572	B	+++	12
4233·25	4233·25	Cr II	31	3·848			
4235·942	4235·95	Fe I	152	2·415	1
4242·38	4242·38	Cr II	31	3·854	4
4246·829	4246·84	Sc II	7	0·314	3
4250·125	..	Fe I	152	2·46	B	++	1
4250·790	..	Fe I	42	1·55		++	
4252·62	4252·63	Cr II	31	3·842	2
4254·346	4254·35	Cr I	1	0·000	1
4258·155	4258·17	Fe II	28	2·693	3
4260·479	4260·49	Fe I	152	2·389	B	+++	1
4260·75	..	V II	18	1·67		..	
4260·75	..	V II	24	1·70		+	
4261·92	4261·94	Cr II	31	3·848	4
4263·836	..	V II	24	1·68	B	..	1
4263·985	..	Fe II			
4264·50	..	V II	24	1·67			
4269·28	4269·29	Cr II	31	3·837	2
4271·159	4271·17	Fe I	152	2·439	B	++	2
4271·764	4271·78	Fe I	42	1·478		+++	
4273·317	4273·33	Fe II	27	2·693	4
4275·57	4275·56	Cr II	31	3·842	3

TABLE III (Contd.)

Wave-length	Solar wave-length	Identification	Multiplet	Lower Ext. Pot.	Blending	Contribution to the blend	Intensity
4278·128	4278·16	Fe II	32	2·680	2
4283·772	..	Mn II	6	5·36	B	..	1
4284·21	4284·23	Cr II	31	3·837		..	3
4286·13	..	V II	23	1·68	B		1
4286·311	4286·33	Fe II			
4287·983	4287·89	Ti II	20	1·075	2
4290·222	4290·23	Ti II	41	1·160	5
4292·246	4292·28 L	Mn II	6	5·36	1
4294·101	4294·15	Ti II	20	1·079	5
4296·567	4296·58	Fe II	28	2·693	5
4300·052	4300·06	Ti II	41	1·175	6
4301·928	4301·93	Ti II	41	1·156	3
4303·166	4303·18	Fe II	27	2·693	—	..	6
4305·715	4305·72	Sc II	15	0·593	—	..	1
4307·900	4307·91	Ti II	41	1·160	B	+++	4
4307·906	4307·91	Fe I	42	1·551		+	
4312·861	4312·88	Ti II	41	1·175	—	—	3
4314·084	4314·09	Sc II	15	0·616	B	++	3
4314·289	4314·32	Fe II	32	2·664		+++	
4314·979	4314·98	Ti II	41	1·156	—	..	3
4316·258	..	V II	23	1·67	B	+	1
4316·807	4316·80	Ti II	94	2·039		+++	

TABLE III (Contd.)

Wave-length	Solar wave-length	Identification	Multiplet	Lower Ext. Pot.	Blending	Contribution to the blend	Intensity
4320·745	4320·75	Sc II	15	0·603	B	++	3
4320·965	4320·96	Ti II	41	1·160		+++	
4325·010	4325·00	Sc II	15	0·593	B	++	4
4325·765	4325·78	Fe I	42	1·601		++	
4330·264	4330·25	Ti II	94	2·039	B	+++	1-2
4330·708	4330·71	Ti II	41	1·175		+++	
4337·049	..	Fe I	41	1·551	B	++	4
4337·33	..	Ti II	94	2·05		++	
4337·916	4337·93	Ti II	20	1·075		+++	
4340·468	4340·48	H γ	1	10·16	20
4344·291	4344·29	Ti II	20	1·079	2
4350·834	4350·43 L	Ti II	94	2·05	B	++	10
4351·764	4351·77	Fe II	27	2·693		+++	
4351·8941	4351·92	Mg I	14	4·327		+	
4351·9056	..	Mg I	14	..		+	
4354·609	..	Sc II	14	0·60	1
4357·574	4357·57	Fe II	2
4362·10	4362·10	Ni II	9	4·012	2
4367·657	4367·68	Ti II	104	2·579	B	..	2
4368·262	..	Fe II	
4369·404	4369·41	Fe II	28	0·766	3

TABLE III (Contd.)

Wave-length	Solar wave-length	Identification	Multiplet	Lower Ext. Pot.	Blending	Contribution to the blend	Intensity
4374.455	4374.47	Sc II	14	0.616	B	++	3
4374.825	4374.82	Ti II	93	2.052		++	
4374.94	4374.95	Y II	13	0.407		++	
4383.547	4383.56	Fe II	41	1.478	B	+++	5
4384.333	4384.32	Fe II	32	2.646		+++	
4384.643	4384.64 L	Mg II	10	9.953		++	
4384.813	..	Sc II	14	0.59		+	
4385.381	4385.39	Fe II	27	2.766	6
4386.858	..	Ti II	104	2.59	1
4387.928	4387.93 L	He I	51	21.13	1
4390.585	4390.58 L	Mg II	10	9.956	B	++	2
4390.977	4391.04	Ti II	61	1.226		+	
4394.057	4394.07	Ti II	51	1.216	1
4395.031	4395.04	Ti II	19	1.079	6
4398.02	..	Y II	5	0.13	B	+	1
4398.314	..	Ti II	61	1.22		+++	
4399.767	4399.78	Ti II	51	1.232	B	+++	3
4400.355	..	Sc II	14	0.60		+	
4402.875	4402.88 L	Fe II	1
4404.68	..	V II	30	1.81	B	+	2
4404.752	4404.76	Fe I	41	1.551		+++	

TABLE III (Contd.)

Wave-length	Solar wave-length	Identification	Multiplet	Lower Ext. Pot.	Blending	Contribution to the blend	Intensity
4411·080	4411·08	Ti II	115	3·081	B	+	1
4411·936	..	Ti II	61	1·22		+++	
4413·600	4413·60	Fe II	32	2·664	2
4415·125	4415·14	Fe I	4	1·601	B	+++	1
4415·559	4415·56	Sc II	14	0·593		+++	
4416·817	4416·83	Fe II	27	2·766	1
4417·718	4417·72	Ti II	40	1·160	3
4418·340	..	Ti II	51	1·23	1
4420·665	..	Sc II	14	0·62	1
4421·949	4421·95	Ti II	93	2·052	1
4433·991	4433·99 L	Mg II	9	9·956	1
4443·802	4443·81	Ti II	19	1·075	5
4450·487	4450·49	Ti II	19	1·079	3
4451·545	4451·55 L	Fe II	2
4455·258	4455·26 L	Fe II	2
4456·650	..	Ti II	115	3·11	1
4464·458	4464·46	Ti II	40	1·156	2
4468·493	4468·50	Ti II	31	1·126	4
4470·864	..	Ti II	40	1·16	1
4471·477	4471·48	He I	14	20·87	B	..	1
4471·688	4471·69	He I	14	20·87			
4472·921	4472·93	Fe II	37	2·832	2

TABLE III (Contd.)

Wave-length	Solar wave-length	Identification	Multiplet	Lower Ext. Pot.	Blending	Contribution to the blend	Intensity
4481·129	4481·14	Mg II	4	8·825	B	++	12
4481·327	4481·34	Mg II	4	8·826		+++	
4488·319	4488·33	Ti II	115	3·110	1
4489·185	4489·19	Fe II	37	2·816	4
4491·401	4491·41	Fe II	37	2·843	5
4501·270	4501·28	Ti II	31	1·111	4
4508·283	4508·29	Fe II	38	2·843	6
4515·337	4515·34	Fe II	37	2·832	6
4520·225	4520·23	Fe II	37	2·795	5
4522·639	4522·64	Fe II	38	2·832	6
4524·732	..	Ti II	60	1·23	1
4533·966	4533·97	Ti II	50	1·232	B	+++	5
4534·166	4534·17	Fe II	37	2·843		++	
4539·62	..	Cr II	39	4·02	1
4541·523	4541·52	Fe II	38	2·843	4
4544·009	..	Ti II	60	1·24	1
4545·144	4545·14	Ti II	30	1·126	1
4549·214	4549·19	Fe II	186	5·885	B	+	12
4549·467	4549·48	Fe II	38	2·816		++	
4549·622	4549·64	Ti II	82	1·577		++	
4552·25	4552·29	Ti II	30	1·111	1
4555·02	4554·99	Cr II	44	4·054	2

TABLE III (Contd.)

Wave-length	Solar wave-length	Identification	Multiplet	Lower Ext. Pot.	Blending	Contribution to the blend	Intensity
4555·890	4555·89	Fe II	37	2·816	7
4558·659	4558·65	Cr II	44	4·056	6
4563·761	4563·77	Ti II	50	1·216	4
4565·78	4565·78 L	Cr II	39	4·025	2
4568·312	..	Ti II	60	1·22	1
4571·971	4571·98	Ti II	82	1·565	5
4576·331	4576·34	Fe II	38	2·832	4
4579·523	4579·51	Fe II	B	+++	3
4580·055	4580·06	Fe II	26	2·572		++	
4580·458	..	Ti II	60	1·23		++	
4582·835	4582·84	Fe II	37	2·832	2
4583·829	4583·84	Fe II	38	2·795	8
4588·217	4588·21	Cr II	44	4·054	4
4589·89	4589·96	Cr II	44	4·055	B	+	2
4589·961	4589·96	Ti II	50	1·232		+++	
4592·09	4592·06	Cr II	44	4·057	2
4595·68	4595·69	Fe II	38	2·843	2
4616·64	4616·63	Cr II	44	4·055	2
4618·83	4618·79	Cr II	44	4·057	3°
4620·513	4620·52	Fe II	38	2·816	2
4625·911	..	Fe II	186	5·93	1
4629·336	4629·34	Fe II	37	2·795	4

TABLE III (Contd.)

Wave-length	Solar wave-length	Identification	Multiplet	Lower Ext. Pot.	Blending	Contribution to the blend	Intensity
4634·11	4634·08	Cr II	44	4·055	3
4635·328	4635·32	Fe II	186	5·930	2
4636·345	..	Ti II	38	1·16	1
4656·974	4656·98	Fe II	43	2·879	B	+++	2
4657·210	4657·21	Ti II	59	1·238		+	
4663·700	4663·71	Fe II	44	2·879	2
4666·750	4666·76	Fe II	37	2·816	2
4670·170	4670·18	Fe II	25	2·572	2
4731·439	4731·48	Fe II	43	2·879	3
4779·986	4779·99	Ti II	92	2·039	2
4805·105	4805·10	Ti II	92	2·052	6
4812·35	4812·36	Cr II	30	3·848	3
4824·13	4824·14	Cr II	30	3·854	8
4836·22	4836·24	Cr II	30	3·842	2
4848·24	4848·25	Cr II	30	3·848	6
4856·19	4856·20	Cr II	30	3·837	2
4861·332	4861·34	H β	1	10·16	20

DESCRIPTION OF TABLE III

The wave-lengths from Moore's revised edition of multiplet table (R.M.T.) of astrophysical interest¹³ (1945) are listed in the first column. Second column contains solar wave-lengths. In this column some of the wave-lengths are followed by a letter 'L' or 'C' which designate the laboratory wave-length and calculated wave-length respectively. In the third column all the identifications are given. Most of these are from the table (R.M.T.) mentioned above. The multiplet

numbers and the excitation potentials for the lower level for the transition producing the line are listed in the fourth and fifth column respectively. A letter 'B' in the sixth column indicates that the bracketed lines were blended and the separation of these could not be easily affected. In seventh column an attempt has been made to designate a rough estimate of the contribution of different members of a blend by the number of *plus* signs. To form an idea one may follow the following key to these estimates:

- +++ Principal contributor,
- ++ Important contributor,
- + Minor contributor.

In many cases when a principal contributor is blended with another very weak line which may be called a very slight contributor the latter has been omitted from the above list. Towards the end of the list only principal contributors could be recognized from the grains as the plates became very weak at this end. In the last column the eye estimates of the intensities of the observed absorption lines are tabulated. In the cases of the blends where the separation could not be affected a combined estimate for the whole blend is given. It may again be noted that these estimates for the lines after $\lambda 4700$ may have a large percentage of error due to personal factor because the plates became quite weak rendering the percentage of the grains quite large.

COMPARISON OF THE SPECTRUM WITH THAT OF α -CYGNI

The present star is classified as cA3 and sometimes also as A2p. α -Cygni is a representative typical super-giant of spectral class of A2. Thus it is supposed to be worthwhile to compare the two spectra. In general features the spectrum of this star resembles closely to that of α -Cygni. The lines of neutral atoms are very weak to make any definite comparison. The absorption lines of ionized atoms are quite similar in shape but they are broader and less deep in this star than the corresponding ones in α -Cygni. To give a definite idea for comparison, the central depths of some of the quite strong absorption lines from the continuum are listed in inches in Table IV for the spectra of both these stars. It may be pointed out here that for this purpose the continuum is placed at 10 inches for both the stars. This table also contains the half-widths of these lines at a point mid-way deep. This half-half-width of a line is expressed in centimeter units for both of them.

A glance at Table IV will show quite conclusively that the foregoing comparative statement is statistically true. Thus one can easily conclude that the two stars are quite similar as far as the absorption line features are concerned. The wings of hydrogen lines are much less than those in α -Cygni. This may be interpreted as due to the fact that probably the present star is more super-giantish in character than α -Cygni.

It is interesting to note that the absorption lines due to neutral helium ($\lambda\lambda 4009, 4026, 4121, 4388$ and 4471) are still present in the spectrum of this star although they are a little weaker than the corresponding ones in the spectrum of α -Cygni. One of them is so weak that it can hardly be recognised. A number of metallic lines due to neutral atoms are present like those in the case of the comparison star but they are also all weaker than the corresponding ones in the

latter spectrum. Neutral manganese lines can hardly be distinguished. Lines due to neutral magnesium are also present but are weak and few in number.

TABLE IV

Comparison of half-half widths and central depths of the absorption lines in the spectra of HD 223385 and α -Cygni

Wave-length	Element	Central depth (in inches)		Half-half width (in cm.)		Lower Ext. Pot.
		α -Cygni	HD 223385	α -Cygni	HD 223385	
4015.50	Ni II	1.40	1.30	0.75	1.0	4.015
4023.388	V II	1.05	0.75	0.85	1.1	1.797
4024.552	Fe II	2.16	1.90	1.35	1.35	4.475
4028.332	Ti II	1.90	1.16	0.95	1.2	1.884
4032.946	Fe II	1.45	0.92	0.70	1.00	4.475
4045.815	Fe I	1.97	1.57	0.85	1.05	1.478
4048.831	Fe II	1.55	1.05	0.90	1.25	5.545
4053.814	Cr II					
	Ti II	2.17	1.50	0.95	1.10	1.885
4063.597	Fe I	1.30	1.00	0.65	0.95	1.551
4067.051	Ni II	2.72	1.65	0.85	1.00	4.012
4071.740	Fe II	1.07	0.85	0.90	0.95	1.601
4077.714	Sr II	1.77	1.30	0.80	0.95	0.000
4101.737	H δ	8.30	6.68	2.50	2.50	10.16
4122.638	Fe II	2.98	1.80	0.80	0.90	2.572
4130.884	Si II	3.93	2.68	0.90	1.05	9.796
4145.77	Cr II	1.10	0.58	1.00	1.25	5.296
4161.524	Ti II	0.71	0.50	0.80	1.00	1.079
4163.644	Ti II	2.43	1.53	0.90	1.05	2.579

TABLE IV (Contd.)

Wave-length	Element	Central depth (in inches)		Half-half width (in cm.)		Lower Ext. Pot.
		α -Cygni	HD 223385	α -Cygni	HD 223385	
4171.897	Ti II	2.38	1.44	0.80	1.10	2.586
4173.450	Fe II	4.90	3.05	0.90	1.10	2.572
4177.70	Ti II	2.71	2.05	0.80	1.10	2.533
	Fe II					
4178.855	Fe II	5.05	3.83	1.05	1.25	2.572
4215.524	Sr II	1.39	0.85	0.90	1.20	0.000
4242.38	Cr II	3.03	2.06	0.70	1.10	3.854
4246.829	Sc II	2.27	1.43	0.75	0.90	0.314
4252.62	Cr II	1.23	0.90	0.75	0.90	3.842
4258.155	Fe II	2.41	2.05	0.85	0.95	2.693
4261.92	Cr II	2.35	2.04	0.75	0.90	3.848
4269.28	Cr II	0.92	0.77	0.85	1.10	3.837
4273.317	Fe II	2.43	1.68	0.80	1.00	2.693
4275.57	Cr II	1.87	1.38	0.80	1.05	3.842
4278.128	Fe II	1.38	0.78	0.85	1.00	2.680
4284.21	Cr II	1.75	1.03	0.75	1.00	3.837
4287.893	Ti II	1.30	0.87	0.75	0.90	1.075
4290.222	Ti II	3.03	2.15	0.85	1.10	1.160
4294.101	Ti II	3.17	2.35	0.70	0.90	1.079
4296.567	Fe II	3.60	2.44	0.80	1.05	2.693
4312.861	Ti II	2.54	1.72	0.80	1.05	1.175
4320.745	Sc II	1.79	1.10	0.85	1.10	0.603
	Ti II					

SPECTRAL CLASSIFICATION

The stars of class A in general are the most difficult ones to classify. In the spectrum of the stars of this class peculiarities are so frequently observed that any sort of accurate classification standard is very difficult to find. 'C' stars and some other peculiar objects make it still more difficult. One finds it a still harder problem when one encounters with the classification of super-giant stars. The best example to reveal this difficulty is the case of ϕ Cas. On the Harvard Henry Draper system it is supposed to be a F5 star whereas on the system of Yerkes Atlas it is designated as A5. In view of these difficulties one can easily say that this classification specially of super-giants is only approximate.

There are several criteria which are applied for the classification of the spectrum at different places. Most of them are applied to the spectrograms of very low dispersion (125 Å/mm.). One of the criteria works quite satisfactorily for stars of main sequence from B0 to F0 is the relative growth of Ca II (K) line with respect to hydrogen lines. It is used in Victoria and Harvard systems.

(i) *Victoria System*.—According to this standard we have

$$\begin{aligned} \text{at A2} \dots\dots\dots & \begin{cases} \text{Ca II (K)} = 0.4 \text{ H}\delta, \text{ or} \\ \text{Ca II (K)} = 0.4 [\text{Ca II (H)} + \text{H}\epsilon] \text{ and} \end{cases} \\ \text{at A5} \dots\dots\dots & \begin{cases} \text{Ca II (K)} = 1.2 \text{ H}\delta, \text{ or} \\ \text{Ca II (K)} = 0.9 [\text{Ca II (H)} + \text{H}\epsilon]. \end{cases} \end{aligned}$$

(ii) *Harvard System*.—This standard is based on the following relation:

$$\begin{aligned} \text{at A2} \dots\dots\dots & \text{Ca II (K)} = 0.4 \text{ H}\delta \text{ and} \\ \text{at A5} \dots\dots\dots & \begin{cases} \text{Ca II (K)} = 0.9 [\text{Ca II (H)} + \text{H}\epsilon] \text{ and} \\ \text{Ca II (K)} \text{ is stronger than H}\delta. \end{cases} \end{aligned}$$

If we apply these criteria for the present star we have from the observations the following relations:

$$\text{Ca II (K)} = 0.5 [\text{Ca II (H)} + \text{H}\epsilon]$$

$$\text{Ca II (K)} = 0.6 \text{ H}\delta.$$

Both these relations give the spectral type between A2 and A3 for ϕ Cas. which agrees very well with the one often used in the previous literature. In spite of this very good agreement, one must not overlook the fact that in the spectrum of such a distant star Ca II lines should also contain a component due to interstellar material between the observer and the star. In many cases quite often one finds that the stars, with many characteristics of F class, have the spectrum in which Ca II (K) line indicates a class of A2 to A3. Even the colours of these stars do not agree with the type obtained from K line. Also in the stars of high luminosity, such as the present one, any study depending on the application of the ratio of the metallic lines to the hydrogen lines must be strongly affected by the absolute magnitude effect. In the region B8 to F0 the hydrogen lines are greatly weakened in super-giants.

Other criterion often used for classifying a spectrum of a star depends on the ratio of the two metallic lines Ca I λ 4227; Fe II λ 4233. This criterion is

used in Harvard system of classification. But in this case also one should note that this does not give a very good criterion because the line Fe II λ 4233 is very much enhanced in the super-giants as is quite clearly seen in the present spectrum. Here the line Ca I λ 4227 is very weak whereas the line Fe II λ 4233 is very strong.

Another criterion, suitable for super-giants, is suggested by Morgan, Keenan and Kellman¹⁴ (1943). They have used the ratio of the two blends $\lambda\lambda$ 4128–4130: $\lambda\lambda$ 4172–4179. Again here we find that it is difficult to use this ratio in case of the spectrograms obtained with high dispersion. It works well for the spectra with very low dispersion where the lines are not resolved. Even for the spectrograms with moderate dispersion like the present ones these blends are resolved into separate lines and then one does not know how to combine them again to get back to the blend strength. Therefore in the present case instead of attempting to find the spectral classification on this criterion it seems worthwhile to estimate the relative differential classification between the star in question and α -Cygni. A very rough eye estimates of intensities of these blends can be made from the same scale intensity tracings of the two stars. It is found that the ratio of the absorption of the two blends for 6 Cas. is very nearly the same as that for α -Cygni which again suggests that the two stars do not differ appreciably in their spectral types.

Barbier and Chalonge¹⁵ (1939) have published two separate curves for giants and main sequence stars representing the relation between the Balmer discontinuity in the observed spectrum and the spectral class of the star. This criterion has also been applied for the study of the present star. Few plates were taken to cover up that region of the spectrum. In this case the Balmer discontinuity in the observed spectrum was found to be 0.4 which agrees well with that found by Margherita Hack¹⁶ (1956). The spectral type obtained from this discontinuity with the help of the abovementioned curves is A 2.5. Thus once again the spectral type between A2 and A3 for 6 Cassiopeia is confirmed.

LUMINOSITY

The wings of the hydrogen lines in HD 223385 are much less than those in α -Cygni which points to the fact that the former is more super-giantish than α -Cygni. Also we find that the absorption intensities of the hydrogen lines in 6 Cas. are much less than those of the corresponding absorption lines in the spectrum of α -Cygni which leads one to the conclusion that the former is brighter intrinsically than the latter. This conclusion is correct only when the spectral types of the two stars compared do not differ appreciably, as is obviously the case for these two stars under consideration in the present note. Otherwise similar effects, which can be produced by the well-known fact that as we advance in spectral types from A0 to A5 the hydrogen lines become less and less in intensity and Ca II (K) line increases in intensity, can also become significant enough to evade any definite conclusive comparison.

At Victoria the intensity of the absorption line H_γ is used to determine the luminosity of a star. Petrie and Maunsell⁴ (1950) have derived a relation between the observed intensity of H_γ and the absolute magnitude of a star. For the present case in the observed spectrum the measured equivalent width of H_γ is 1.92. Using Petrie's curves, one finds that this corresponds to a spectroscopic absolute magnitude of -7.1 . Thus the absolute magnitude for this star as derived by Petrie and Maunsell by the same method is confirmed once again.

ELECTRON PRESSURE

The electron pressure can be determined approximately from the English Teller formula¹⁷ (1939). The electron density is related to the number of stark broadened hydrogen lines in the Balmer series which can be resolved from the confluence of their wings. In case of the present spectrum these lines were resolved up to H_{28} . Thus applying the formula one finds that the corresponding electron density would be of the order of 10^{12} . The electron pressure thus obtained from the density of electrons is of the order of unity. The electrons pressure can also be obtained from the study of the curve of growth for the metallic lines. When such a study has been carried out for this case for absorption lines of neutral and ionized iron the electron pressure from this analysis is of the order of a hundred. A similar disagreement between the electron pressure found for hydrogen lines and for the metallic lines was also noted before by Buscombe¹⁸ (1951) in the analysis of A type stars. A satisfactory explanation for this discrepancy is not yet known.

DOPPLER VELOCITIES

The limitations of the curve of growth-method are well summarized by Wright¹⁹ (1947). The author has determined elsewhere²⁰ the turbulent velocities of small and large eddies following Huang and Struve²¹ (1952) applying the relationship between the equivalent width and the 'half-width' of the absorption lines in the spectrum of a star. The equivalent width is affected by small eddies only where as the 'half-width' is influenced by both types of eddies. The curve of growth method gives the velocities of the small eddies while the profiles of the absorption lines represent motion of both kinds of eddies.

In the case of the present star the velocities thus obtained are 15 km./sec. for the small eddies and 30 km./sec. for the large eddies. It may be remarked here that this velocity of small eddies is in good agreement with the velocity obtained from curve of growth analysis as it should be expected. There seems to be no variations of velocities with different excitation potentials for one element or for different elements in the case of the present star. In this investigation absorption lines of Fe II, Cr II and Ti II are used. For other elements sufficient number of lines were not available.

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